MÉMOIRES

H. ÉMILE ESCHINAZI

THE USE OF THE DIENIC ADDUCTS IN THE SYNTHESIS

OF

CARCINOGENIC COMPOUNDS

RELATED

TO THE PHENANTHRENE

MÉMOIRES

DE

L'INSTITUT D'ÉGYPTE

—

TOME QUARANTE-HUITIÈME

MÉMOIRES

PRÉSENTÉS

A L'INSTITUT D'ÉGYPTE

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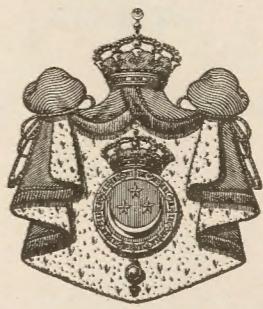
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THE USE OF THE DIENIC ADDUCTS

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RELATED TO THE PHENANTHRENE.

———

PART (A).

Introduction.—The production of tumors by means of pure chemical agents is known already for nearly a quarter of a century and in most of the laboratories where the clinical study of the cancer constitutes the main part of the researches, methyl cholanthrene or benzopyrene are used in this effect to the same extent as stilboestrol is in use in the laboratories dealing with oestrogenic compounds.

In fact, a carcinogen is a pure chemical compound which is able, when applied in a suitable manner to the living body (parenterally in most of the cases), to produce tumors which can be transplanted like in the cases of the spontaneous cancer. The blastogenic activity of such a compound is measured by comparison with well known carcinogens in a way which is similar to that of the international units when applied to the hormones. The physiological experiments dealing with the carcinogens are, however, more laborious since the production of carcinoma occurs, mostly, within a period which may extend for weeks or years, following a prolonged treatment with the carcinogen in a suitable form.

The facts which called the attention of the scientists to the possibility of a chemical carcinogenesis, were undoubtedly those of tumor production noticed repeatedly among workers dealing with coal tar distillation. The active substance suspected was shown to be a derivative of the anthracene. Since then, many polycyclic hydro-carbons were synthesized, but only a few of them proved to have a blastogenic activity.

The mechanism of the tumor production by pure chemical reagents is still an object of controversy. As stated by F. Bergmann[1], in 1942, it is very likely that only the shape and size of carcinogens may determine their activity, and owing to their mostly

aromatic monoplanar structure they seem to be adsorbed by one and the same acceptor in the living cell. It is, indeed, worthwhile to point out that, unlike other biologically active chemical substances, the most potent carcinogens are characterized by their chemical inertness and stability and the absence of polar groups (i. e. OH; OCH_3, Cl, NH_2, etc.) which mostly diminish or destroy their activity even when they are at positions where methyl groups exert a strong blastogenic influence. All carcinogens are thus conceived as parts of an "ideal carcinogenic structure" which presumably would exhibit a maximum activity because of its complete adaptation to the supposed acceptor. The maximum of activity seems, indeed, to occur in those polycyclic compounds where the length of the basal skeleton reaches the anthracene whereas those of a smaller one such as a naphtalene skeleton as well as a bigger one such as a naphtacene skeleton are slightly or not at all active. This favors unquestionably the hypothesis of a suitable adsorption on the living cells which seems to be directive to carcinogenic potency in these hydrocarbons.

On the other hand, it is known that alkyl substituents show a different influence on the activity of the parent ring structure according to their position. In this way they can enhance, inhibit or undisturb the tumor production. A rule was established stating that side chains produce active carcinogens, if they imitate rings which enhance carcinogenesis and *vice-versa*. Following F. Bergmann's [1] hypothesis, it seems that chemical carcinogenesis is really a prevention of a normal process caused by the disturbance of the cell division on the body by means of a mechanical burdening of some part of the division apparatus thus producing the same effect as Xrays on the division apparatus of the living cell.

1. *The synthesis of 1, 2, 3, 4 dibenzphenanthrene and its derivatives.*—In our present work we tried to synthesize 1, 2, 3, 4 dibenzphenanthrene (I) the activity of which was predicted in 1938 by Hewett [2] from the behaviour of 1 and 2 methyl 3, 4 benzphenanthrene (I_A and I_B) :
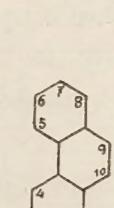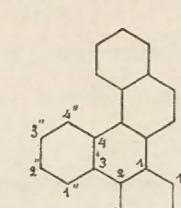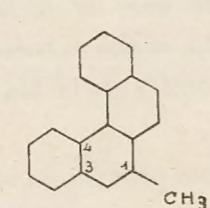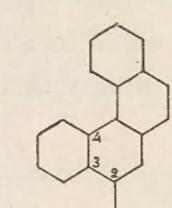
Phenanthrene   1 I_A I_B

The activity of I serves as an excellent example for the correlation that exists between the geometrical form of a molecule and its blastogenic properties.

If however carbon atoms 4' and 1" are connected by a two carbon bridge as in II (dotted line) a derivative of the strong carcinogen 9.10 dimethyl 1.2 benzanthracene is obtained (a similar idea has recently been expressed by Bachmann) [3].
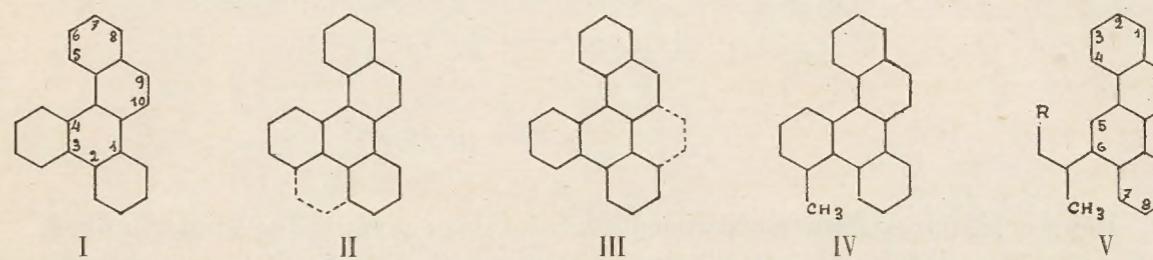
I   II   III   IV   V

In a similar way by a bridge between 1' and 10 the very potent carcinogen 1, 2, 3, 4 dibenzpyrene (III) is formed. As an approach to the synthesis of (II) we have tried to prepare 1" methyl 1, 2, 3, 4 dibenzphenanthrene (IV.)

Finally, if the 4-4" bridge of (I) is opened we get an alkyl derivative of 6 chrysene (V). In this connection, as well, we synthesized some iso-alkyl derivatives of 6 chrysene in order to test their carcinogenic potency which is supposed to be related to the structure of the cyclic carcinogen they imitate (see the synthesis of the stylbene derivative (VI) which imitates that of benzopyrene (VII) both being strong carcinogens) [4].

VI   VII
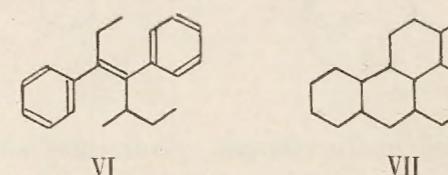
2. The synthesis of I was accomplished by Hewett [2] by the application of the Pschorr method to α (9 phenanthryl o nitro cinnamic acid).

Diazotation - CO_2
(Pschorr)

1.
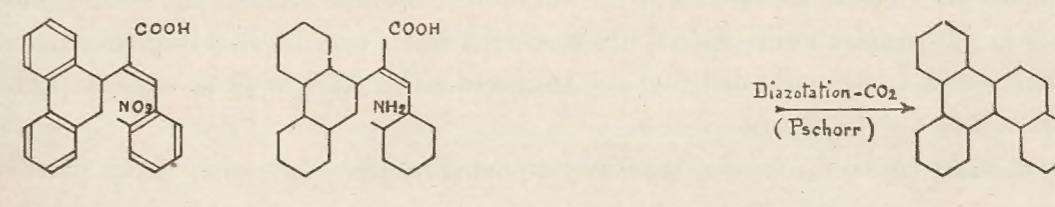
We wish to describe some new ways, which promised a much shorter synthesis than that achieved by Hewett.

If I is opened at C_9-C_{10}, the resulting structure can be obtained from the diene reaction of dicyclohexenyl with phenyl substituted olefines (see part B of this work).
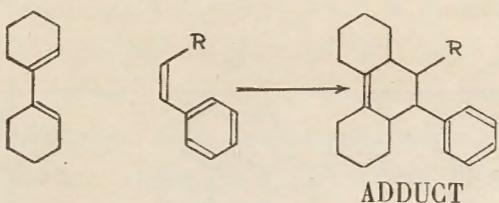
ADDUCT

However all our cyclization experiments failed at some point. The adduct in which $R = COCH_3$ could not be reduced to its corresponding alcohol. Likewise we did not succeed in lengthening the carboxyl side chain of the adduct in which $R = COOH$, by the Arndt-Eistert Method to yield the corresponding acetic acid $R = CH_2 COOH$.

If the skeleton of I is opened in C_2-C_3, 1-2 diphenyl naphthalene is obtained. In order to reverse this procedure we attempted to cyclize VIII or IX both obtained from 2 phenyltetralone and o. chloro phenyl magnesium Iodide in a Grignard reaction with

VIII   IX
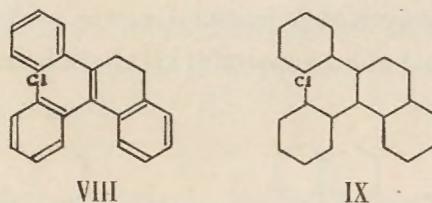
subsequent dehydration and dehydrogenation. Both compounds resisted all reagents which could cyclize by removing a molecule of H Cl such as molten KOH; or $AlCl_3 +$ NaCl mixture at 150°.

Our observations can hardly be explained since the cis-structure of VIII is guaranteed by its cyclic structure. Therefore cyclization should be expected as in the case of o. chloro cis stilbene derivatives [5]. Moreover, since the aromatically bound chlorine is highly reactive under special conditions (it reacts with Li. in a cold suspension of Ether) it is safely concluded that the failure of either VIII or IX to undergo cyclization is not due to sterical reasons.

By opening I at C_1-C_{11}, o—(α Naphthyl) diphenyl results. Inversion of this process

may be achieved by several new routes. The one selected by us was the Grignard reaction of cyclohexenyl-cyclohexanone [6] with α-Naphthyl Magnesium bromide. The carbinol obtained (X) was cyclized by means of $AlCl_3$ or $SnCl_4$ in benzene rather than in carbon disulfide solution. The reaction product is composed at least of two compounds which represent different kinds of cyclization with different stages of Hydrogenation (Disproportionation). The main product was found to consist of the spirane (XI_A) and probably traces of the hydrogenated dibenzphenanthrene skeleton (XI_B)

X XI_A XI_B
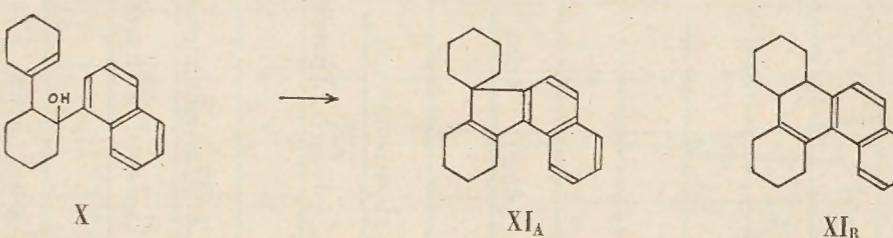
which could not be isolated. Two characteristic picrates were obtained. But only the corresponding hydrocarbon of (XI_A) reacted with selenium at 320/340° to yield (XII) which exhibits a strong green fluorescence. The latter was oxidized to its quinone (XIII.)

XII   XIII   XIV   XV
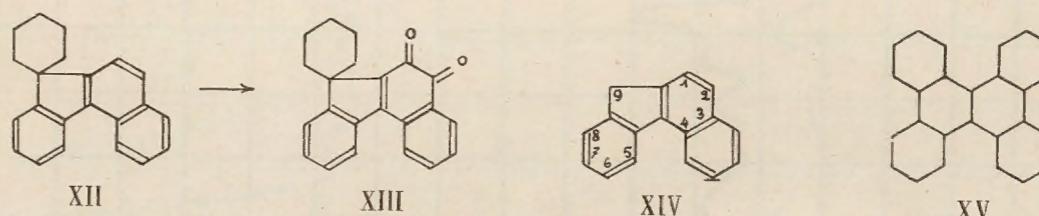
The exact structure of this benzospirane derivative (XII) was disclosed spectrographically thanks the kind collaboration of Dr. R. Norman Jones from America to whom we are indebted for the following spectrographical data.

(XII) and (XIII) show a great fall in absorption intensity between 3500-3600 A° which is suggestive of a benzfluorene derivative (XIV) and the region of the curves between 2400-3600 A° show a great similarity with the curve of 3.4 benzfluorene (XIV) [7], on the other hand the curve of (XII) shows no resemblance to either of the two structures of 1.2.3.4 benzphenanthrene which contain the chrysene and the 3.4 benzphenanthrene chromophores [7]. The presence of the spirocyclohexane ring, following Dr. R. N. Jones assumption, has probably little effect on the spectrum [8].

Wave length

5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8 Log. E Molar
2.6
2.4
2.2
2.0
1.8 Wave length (Å)
1.6 2400 2600 2800 3000 3200 3400 3600

2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
      3800 4000 4200 4400 4600

----- Hydrocarbon
XII
(Solvent Ethanol)

——— 3.4 Benzofluorene
(Solvent Ethanol)
XIV

(Copied from Maynœrd & Roe
(proc. Roy. Soc. A 158, 634, 1937)

——— Chrysene
                              Copied from
----- 3.4 Benzphenanthrene Maynœrd & Roe
(Solvent ethanol)   (Ibid.)

5
4.8
4.6
4.4
4.2
4
3.8
3.6
3.4
3.2
3
2.8
2.6
2.4
2.2
2
1.8
Log. E/ Molar
Wave length (Å)
      2400 2600 2800 3000 3200 3400 3600 3800 4000

— 7 —

As a further application of the method just described, we studied the interaction of cyclohexenyl-cyclohexanone with 9 phenanthryl magnesium bromide. The mixture obtained which consisted of a different kind of cyclization and dehydrogenation products was fractionated and the highest boiling fraction used for dehydrogenation with selenium. A slow reaction occurred at $335/345°$ yielding a mixture of various dehydrogenated stages amongst which a small amount of the completely aromatized tetrabenznaphthalene (XV) which was identified as its black picrate.

3. For the synthesis of IV we used chrysene as starting material since I can be regarded as the 5,6 benzochrysene.
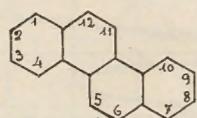
CHRYSENE   I   IV
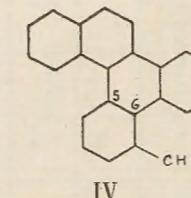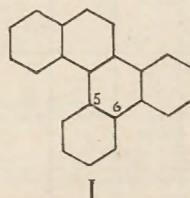
a) From the Friedel and Crafts reaction of chrysene with acetylchloride we isolated in addition to the two isomeric monoacetyl derivatives mp. 156° and mp. 254° described by Funke [9], a diacetyl derivative mp. 296°. The main product of the reaction being, however, the 6 acetyl chrysene while the second monoacetyl isomer owing to its high melting point 254° is supposed to be the 2 substituted product. This hypothesis is based on the fact that the 5 position of the acetyl ascribed by Funke to this isomer was discredited by the fact that its reduction product did not correspond with the authentic 5-ethyl chrysen prepared by Newman [10]. Our assumption that substitution occurred in the 2 position is based on the fact that the 1 and 2 alkyl derivatives of chrysene have the highest melting points of all isomers [11] and also that the reduction product of this isomer is not identical with 1 ethyl chrysene [11]. It will be of interest to see if the diacetyl derivative isolated by us has a symmetrical structure like e. g. the disubstitution products of Pyrene and Perylene in the Friedel-Crafts reaction, or represents a combination of the two mono substituted derivatives.

b) Grignard reaction of 6 acetyl chrysene with methyl magnesium Iodide gave a mixture of the carbinol XVI and the diene XVII.

Conversion of XVI to XVII must be carried out with great precaution, because gentle heating with acids causes poly(di-?)-merization. The best method for dehydration consists of adding a few drops of concentrated sulphuric acid to a cooled solution of XVI in acetic acid. If the same reaction is carried out at 100°, a polymer hydro-

carbon m.p. 307° is obtained, which results also from heating XVII with $SnCl_4$.

c) Diene reaction of 6 isopropenyl chrysene (XVII) with maleic anhydride was tried under a variety of conditions, until the most suitable method was detected. When the diene was heated with five equivalents of the anhydride on a steam bath, the
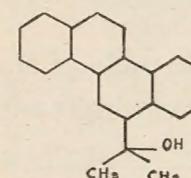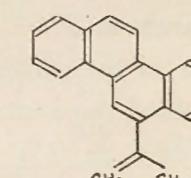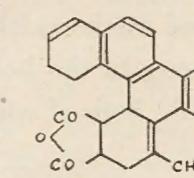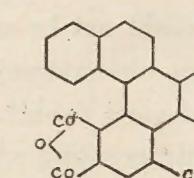
XVI   XVII   XVIII   XIX

polymer m.p. 307° was the only reaction product. Xylene as solvent yielded the desired adduct XVIII is unsatisfactory yield. In view of the easy dehydration of XVI, we tried to melt it together with maleic anhydride at 120° and, indeed, we obtained XVIII in 40 % yield. Finally it was found that in boiling acetic anhydride the diene condensed in 75 % yield. The simple method consists of boiling the carbinol XVI with maleic anhydride in acetic anhydride; the adduct results in 80 % yield. XVIII exists in two polymorphic modifications of identical m.p. and mixed m.p. but of different solubilities. From hot superconcentrated solutions, prisms are obtained, whereas diluted solutions deposited needles. Formula XVIII, which we ascribe to the adduct, contains the double bond in its "original" position, although a shift of this bond to restore the disturbed aromatic chrysene skeleton could be expected. However, only form XVIII explains the easy redissociation into the components, when the adduct is heated above the m.p. especially in the presence of Zinc dust.

d) Aromatisation of XVIII with lead tetraacetate gave a 20 % yield of 1″ methyl 1-2-3-4 dibenzphenanthrene 3″-4″ dicarboxylic acid anhydride XIX but this product could not be completely decarboxylated to the desired hydrocarbon IV. With basic copper carbonate, partial decarboxylation occurred, leading to a monocarboxylic acid XX (*a* or *b*) [12]. Aromatization with bromine gave XIX in impure form.
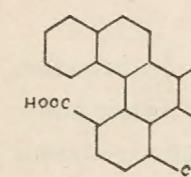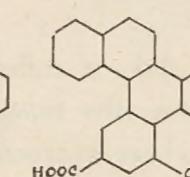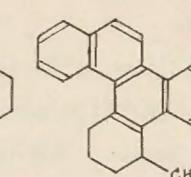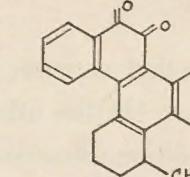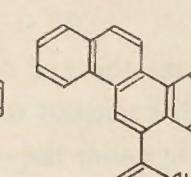
XX *a*   XX *b*   XXI   XXII   XXIII

We now attempted to reverse the order of reactions, carrying out decarboxylation before aromatization. KOH or CaO gave only tarry products. When, however, the adduct was heated directly with selenium to $260°$, complete decarboxylation took place prior to dehydrogenation, the product, obtained in 50 % yield being the tetrahydroderivative of IV probably (XXI), which was characterized as its quinone XXII but could not be aromatized further with selenium at $360°$.

This observation is contrary to the behaviour of the corresponding adducts of α and β vinyl naphthalene [13] both of which yielded the aromatized anhydrides with dehydrogenating agents.

4. Dealing now with the synthesis of the alkyl homologues of V and XXIII which, we assume, will produce active carcinogens in the measure that their side-chains imitate active cyclic structures, it is worthwhile to point out that, in a plane, a methyl group has only one position available, an ethyl group one to two, a n-propyl residue 2-4, a n-butyl group 4-8. (The maximal number of possibilities depends not only on the length of the side chain, but also on the structure of the substituted cyclic compound and on the point of substitution. Therefore maximal and minimal numbers are given in every case.) The probability that a side chain will occupy just the desired "pseudocyclic" position, thus decreases with increasing chain length. This conclusion is in agreement with the experiments of Cook [14] on 5, n-alkyl 1.2. benzanthracenes. The branching of the aliphatic chains modifies the described effect. An Isopropyl group has only one possible position, the sec. butyl group 2-4, the sec. amyl 6-8 etc. For unsaturated radicals like in XXIII the number of possibilities is still further reduced to half by the fixed arrangement regarding the double bond.

To test this hypothesis, we have prepared by means of Grignard reactions with 6 acetyl chrysene a series of homologous hydrocarbons (XXIII) where R=H; CH_3, C_2H_5, $n\,C_3H_7$; and also the corresponding saturated compounds of V where R=H; CH_3. From table I it is seen that the m.p's. fall very rapidly with increasing chain length, and it may be, that the higher members of the series represent a mixture of the cis and trans. forms.

Like the α, β dimethyl styrene, XXIII with R=CH_3 did not suffer polymerization by hot mineral acids. On the other hand it is also unreactive towards maleic anhydride under the conditions described above. All the above hydrocarbons are under investigation for carcinogenic tests in the cancer laboratories of the Hebrew University, Jerusalem.

TABLE I.

ALKYL CHAIN	COMPOUND XXIII	M. P.	M. P. OF PICRATE	COMPOUND V	M. P.	M. P. OF PICRATE
R = H	$C_{21}\,H_{16}$	$161°$	$144°$	$C_{21}\,H_{18}$	$137°$	$144°$
R = CH_3	$C_{22}\,H_{18}$	$160°$	$132/3°$	$C_{22}\,H_{20}$	$100°$	$133°$
R = C_2H_5	$C_{23}\,H_{20}$	$102°$	$138/40°$	—	—	—
R = $n\,C_3H_7$	$C_{24}\,H_{22}$	$40°(?)$	$129/30°$	—	—	—

ON THE STERICAL COURSE

AND THE MECHANISM OF THE DIENE REACTION.

PART (B).

Introduction.—The diene reaction, commonly known as the Diels and Alder reaction, was discovered as early as 1906 by Albrecht[19] when he noticed that cyclopentadiene gave mono and di-addition compounds with p. benzoquinone. Later, in 1920, Euler and Josephson[20] succeeded, in a like manner, to condense isoprene with p. benzoquinone to give the symmetrical bis-diadduct, which proved to behave like an aliphatic diketone. But it is only since 1928, that a particular attention was given to this new type of addition reaction, when the active works of Diels and Alder (and especially Alder)[21] shed a certain light on this simple and most elegant new way of providing chemical change. The richness and the variety afforded by the diene reaction have been exhaustively utilized, since then, in the synthesis of almost an unlimited number of hetero.-and polycyclic compounds.

Some interesting synthesis involving the diene reaction are given below :

a) *Heteroclyclic* (Diels and Alder)[21].
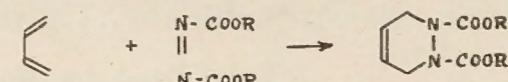
butadiene + Azodicarbonester.

b) *Polycyclic* (Fieser)[22].

CHRYSENE
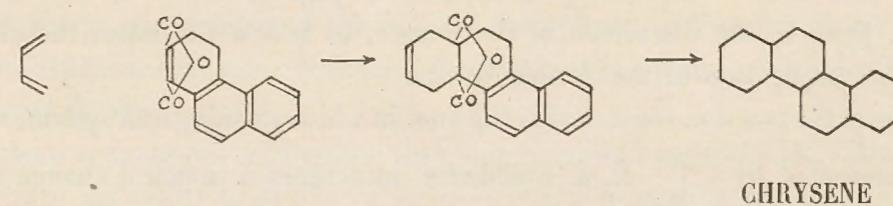
c) Hormone-like products (Goldberg and Muller) [23].

2 Isomers.

compare with OESTRONE
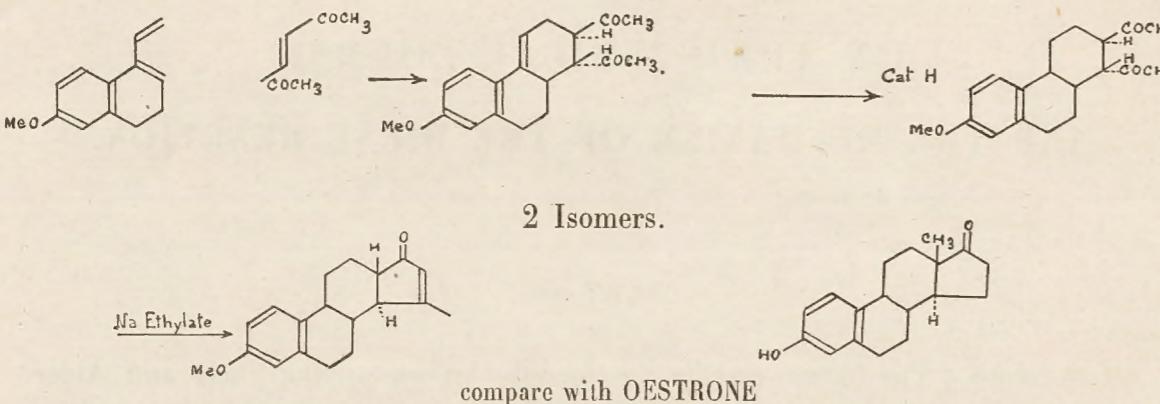
The methoxy compound had oestrogenic activity and, if it is supposed that the trans diacetylethylene maintained its structure during the diene reaction (Trans H:H), it is logical, assume the authors, that such trans-configuration should also be present in the oestrone itself. (Trans CH_3:H).

d) Carcinogenic compounds related to the dibenzphenanthrene series. (In part A of our present work.)

Methyl Tetrahydrodibenzphenanthrene.
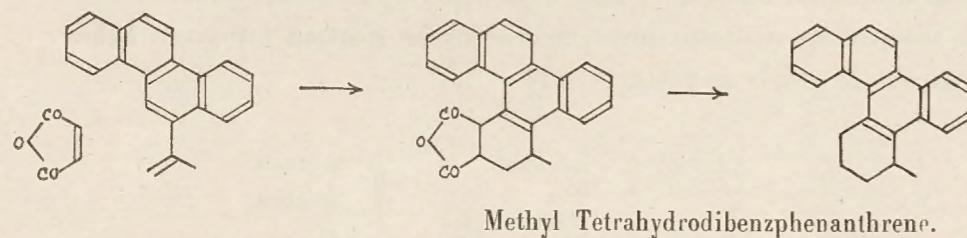
1. *The diene reaction : a) Conjugated systems.*—The study of the mechanism of the diene reaction involves necessarily that of the conjugated double bonds, and it is necessary, prior to the discussion of the former, to review the latest theories concerning the conjugation of the double bonds.

The type of the reaction concerned is the one, in which a conjugated system, schematically represented by : ⟨ (i. e. butadiene) undergoes a chemical change with an

activated, unsaturated compound (such as ethylene): represented by ‖ to give an addition compound, or *adduct,* containing a new six membered ring, partly unsaturated thus :

cyclohexene ring.
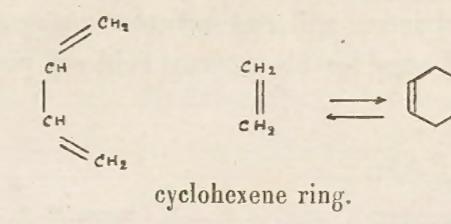
Both the conjugated system, known as the *diene,* and the unsaturated ethylenic compound, known as the *philodiene,* are under the influence of their own substituents which play their part in promoting the activation of the double bonds; since it is fairly known that, only when suitably activated, these compounds may undergo a chemical change or reaction.

It is noteworthy to point out that activation can also be induced *by mere* pressure and temperature. In this connection Joshel and Butz [24] in 1941 noticed the presence of some cyclohexene when butadiene together with ethylene, were submitted to high temperature and pressure.

What is known about conjugation of unsaturated compounds, has been dealt with a long time ago, when Griner [25], in 1893, discovered that butadiene with bromine gives, on standing, a solid dibromide, m. p. 53/4°, which was shown by Thiele [26], in 1899, to contain the 1,4 addition product. The famous work of Thiele involving the residual valencies need not be emphasize but the most predominant fact to be noted in it, being the special tendency of the conjugated systems to give terminal addition compounds (1, 4 in the case of butadiene) and, also, the fact, that the energy content of such systems, is by 10 Cal/Mol lower than that of the isomeric non-conjugated dienes.

It is now admitted that such properties of the conjugated systems depend on the possibility of ionizing the successive double bonds, and then, recombining the ionic charges between adjacent atoms, in such a way, that an electronic charge can migrate from end to end of the system. The direction of migration will then be determined by the pressure of electrons at the ends of the system, so that the dipole moments of the substituents may again become a predominant factor in determining the course of chemical change.

The characteristics of the alternate single and double bonds of a conjugated system is, therefore, its ability to develop a series of alternate positive and negative charges

on alternate atoms and this spread of polar activation throughout the whole chain of atoms, provides an electrostatic analogue of a chain of magnets, neutralizing one another in the middle, without weakening the terminal poles. In the middle of the system the lines or tubes of forces will run between contiguous atoms, and will be almost entirely closed; but a considerable external field will persist round the terminal poles.

$$C=C-C=C \rightleftharpoons \overset{+}{C}-\overset{-}{C}-\overset{+}{C}-\overset{-}{C} \rightleftharpoons \overset{+}{C}-C=C-\overset{-}{C}$$

$$H_2C \quad\quad C \quad\quad C \quad\quad CH_2$$
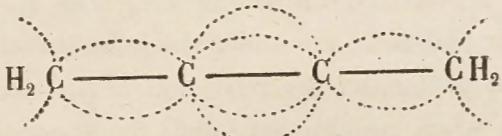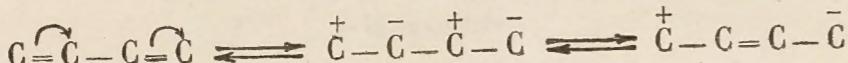
However, Lapworth and Robinson [27] in 1922 regarded it as improbable that any molecule should be activated simultaneously at more than one point at the same instant; thus depicting : $\overset{+}{C}-\overset{-}{C}-\overset{+}{C}-\overset{-}{C}$ should be written in general :

$$C=C-C=C-C=C \longrightarrow \overset{+}{C}-C=C-C=C-\overset{-}{C}$$
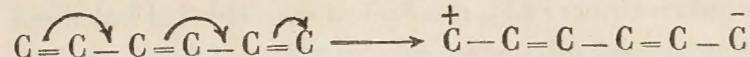
The arrow ⌒ shows a transfer of a pair of shared electrons.

The primary process is, probably, a collision between an ion (or ionizable molecule) of the reagent and one atom of the double bond, giving rise to a local ionization, which is spread all over the chain by means of this electronic transfer. Such an activated molecule can suffer, either a deactivation or a chemical change. The new arrangement of bond, whereby a pair of a valency electrons is handed over from end to end of the chain, enables the neutralization of the opposite charges of an ionized reagent in the process of *terminal* addition, as well as, in the more normal process, of a "Vicinal addition" (i. e. 1.2 or 3.4 addition).

Not only $C=C$ or $C=O$ groups can form part of a conjugated system, but also any element, which is able to form a double covalent bond or, in other words, which possesses unshared electrons, for example N or S. The most typical conjugated systems concerned here are :

1) *Polyenoid Systems* : $C=C-C=C-C=C-C=C$... etc.

2) *Katioenoid Systems* (or crotonoid) : $C=C-C=O \rightleftharpoons \overset{+}{C}-C=C-\overset{-}{O}$.

3) *Discordant (or crossed) polar systems* : $O=C-C=O \rightleftharpoons \overset{-}{C}-\overset{+}{C}-\overset{+}{C}-\overset{-}{O}$
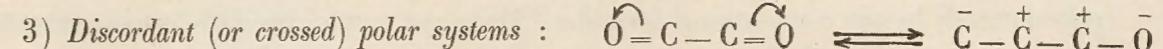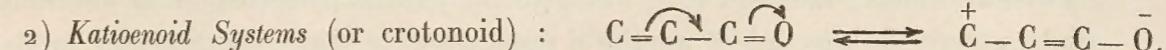
type of Maleic anhydride.

$$O=C \quad C=C-C=O$$
$$\Updownarrow$$
$$\overset{-}{O}-\overset{+}{C}-\overset{+}{C}-C=C-\overset{-}{O}$$
$$\overset{-}{O}-C=C-\overset{+}{C}-\overset{+}{C}-\overset{-}{O}$$
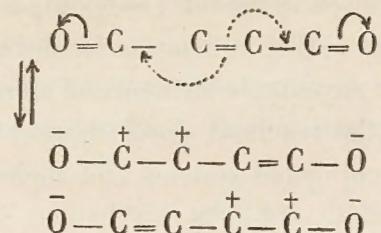
1) Is typical to the dienic compounds; 2) 3) and 4) are typical to the philodienic compounds.

Like Thiele who regarded conjugation as conductive to molecular stability, Ingold in 1933 [28], introducing the conception of wave mechanics, stated that an electron has not an exact location, and its charge may be shared over many atoms so that conjugated systems could be represented as entities in resonance, having a distributed charge, in the perturbed state, with a small external field, and a lower energy content than in the unperturbed one. This tendency to lose energy in passing form

$$\text{Unperturbed state} \xrightarrow[\text{energy}]{\text{loss of}} \text{Perturbed state}$$
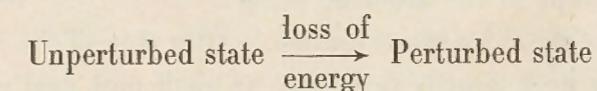
initiates the electromeric change in the conjugated systems. This spread of polar activation is also described, by Ingold, as the mesomeric effect. The resulting molecule has orbital vibrations, of the different electrons, coupled together and is in state of *Resonance*. (Following Pauling's suggestion, a molecule should be considered in state of Resonance when a continous and very rapid oscillation occurs between two forms within a period shorter than 10^{-8} sec.)

The mesomeric effect is essentially stabilizing. Thus, one can suppose that the electromeric change in a conjugated system follows a polar activation, because the ion, initially produced, has a higher energy content than the ion produced subsequently by electronerization. The coupling of the electronic orbits, after Ingold, provides also an explanation of why the activation of a carbonyl group of C_2-C_3 unsaturated ketones is followed by the activation of the double bond, without further increment being required, i. e. :

$$C=C-\overset{+}{C}-\overset{-}{O} \quad \text{gives promptly} \quad \overset{+}{C}-\overset{-}{C}-\overset{+}{C}-\overset{-}{O} \text{ or } \overset{+}{C}-C=C-\overset{-}{O}.$$
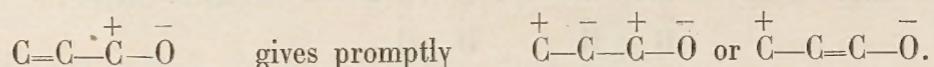
Physical evidence indicates that, owing to the mutual perturbation of electronic orbits, a molecule may indeed acquire a resonnance structure, which cannot be depicted exactly by any conventional formula. Many spectrographic data (measurements of the energy levels in the infra red) support this conclusion, and Pauling[29] showed, indeed, in 1931, that in many molecules the actual heat of formation is less than that calculated for any simple structure of simple covalent link. This perturbation affects the value of the resultant dipole moment and explains the great stability of many neutralized conjugated systems and their chemical properties, such as the carboxyl

and the nitro group — $C \begin{smallmatrix} O \\ O-H \end{smallmatrix}$ $\qquad -\overset{+}{N} < \begin{smallmatrix} O \\ O \end{smallmatrix} \Bigg\} \ominus$ and also the stability
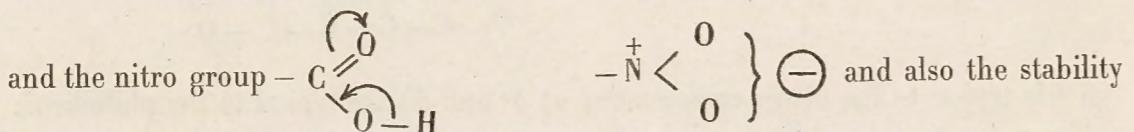
of aromatic ring compounds and the free radicals such as triphenyl methyl.

In their optical behaviour, the conjugated systems show a new type of lower frequency absorption, below the one typical to unsaturated compounds, which lies in the 1850 A. U. region. This absorption ranges even in the visible, when the polyenoid system contains more than four conjugated bonds. In addition, the molecular refractions of the conjugated systems show, generally, the phenomenon of optical exaltation, except in the aromatic series.

b) *The mechanism of the 1.4 addition reaction.*—After that all the features of the conjugated systems have been shortly reviewed, we shall now deal with the possibility of the latter to undergo chemical change with the philodiene, which must be substantially an unsaturated (olefinic) compound, the activation of which being *usually* promoted by an hetero atom, such as an electron acceptor (N, S, O) or, to some extent, by other groups, connected to it and liable to set on an electromeric change. The order of effectivness, given by Kermak and Robinson[30] in 1922, being that of the diminishing strength of bases :

$$\overline{NH} > \overline{O} > NH_2 > OH > OAc > I > Cl,$$
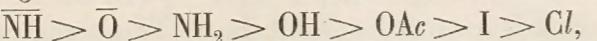
which is, also, the order of mobility of the lone pair of electrons. Addition reactions in unsaturated systems may sometime be due to symmetrical *non-polar rupture* of one of the two shared duplets of the ethylenic bonds. In such *non-ionic* reaction, both the free neutral radicals formed possess and odd unpaired electron, and become the centre of attack.

$$CH_2 = CH_2 \longrightarrow \overset{H}{\underset{H}{\overset{..}{C}}} :: \overset{H}{\underset{H}{\overset{..}{C}}} \longrightarrow \bullet \overset{H}{\underset{H}{\overset{..}{C}}} : \overset{H}{\underset{H}{\overset{..}{C}}} \bullet \longrightarrow \ldots H_2C—CH_2 \ldots$$
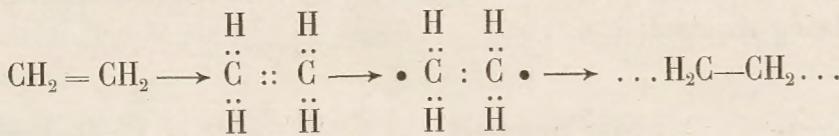
This kind of reaction is characteristic in gases and in non-ionizing solvents (benzene, carbon tetrachloride, etc.) where the very small dielectric constants of the media makes the formation of ions very difficult. In these cases, the energy required for the symmetrical fission of the duplet is not derived by an electrostatic field, but may be obtained from radiation, or from intermolecular collisions giving rise to a small proportion of molecules of high energy content in accordance with Maxwell's law of distribution of energy. The final rupture of the molecule depends on the concentration in the vibrational energy of a particular bond.

Ionic reactions, on the contrary, are characteristic of solutions of high dielectric constants (e. g. water) and, unlike the non-polar ones, they are influenced by the electrical environment of the medium such as reagents, catalysts or surfaces of a polar nature. In such cases, there is an unsymmetrical or *polar fission* of one covalent bond of the ethylenic link giving rise to a pair of reactive ions with opposite charges and sharply differenciated combining properties, e, g. The carbonyl group $C = O \rightarrow \overset{+}{C} = \overset{-}{O}$; where $\overset{-}{O}$ is fairly stable while $\overset{+}{C}$ is very reactive and adds $\overline{CN}$ groups, etc.

The *Kationoid* character is very pronounced in the philodiene, since the activation promotors (O, N, S) are electron acceptors and are fairly stable as anionoids, while C, because of its unstability, becomes the centre of attack.

The *anionoid* character in an olefine or in the diene system is more pronounced than its Kationoid one. For example, if an olefine is ionized it may yield two actives poles, the negative of which being probably the most reactive.

$$C = C \rightarrow \overset{+}{C} = \overset{-}{C}$$
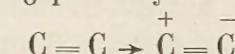
since it seems that the reagents producing negative carbon atoms are less numerous and less easy to prepare.

The above considerations regarding the diene and the philodiene and their polar activation, have set a number of theories concerning the 1.4 addition in the diene reaction.

Robinson and Cow[31] in 1941, claimed, in some cases, a smooth reduction of the philodienes, acting as electron acceptors, by the dienes, which are anionoid in character and act as electron donors in their carbons C_1-C_4 : the general scheme being :

ISOEUGENOL   ISOSAFROL

(Dotted lines indicate the movement of a single electron).

3.
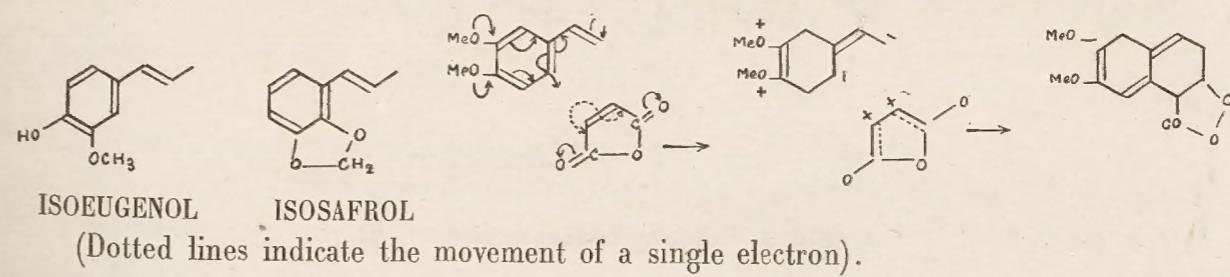
The complex formed, after the addition, restores the adduct by relieving the strain produced by the transfer of electrons.

Such a scheme is, however, unadequate for philodienic compounds, possessing only one promoting group, and also for dienes which, unlike isoeugenol and iso-safrol, possess no polar substituents such as $\overset{+}{\text{O}}$. The same reaction should, therefore, proceed by different mechanisms, in different cases. One of them, would require the bipolar approach, in the activated forms, of the diene and the philodiene; for example :
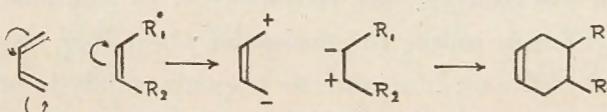

Fig. 2.

Such a device, however, is not enough explanatory. For example, the polarization of the olefinic bond, in the philodiene is not easy to depict by a mere movement of the shared duplet itself, but has to be initiated through the activation promoting groups. Besides, the opposite and polar character of the ionized neighbouring carbon atoms of the philodiene must be so strongly pronounced as to induce a suitable ionization of a *symmetrical* diene during the bipolar approach. An unsymmetrically substituted philodiene, like acroleine, can possibly explain such a process but a symmetrical one like maleic anhydride, would acquire a hydrid polar from which is unable to explain such an induction. Actually, the highest reactivity of maleic anhydride towards symmetrical or unsymmetrical dienes discloses the weakness of such a scheme.

In our opinion, the primary process is probably a collision between the ionizable molecule of the philodiene and one atom of the double bond of the diene giving rise to a local ionization in the diene, which is spread all along the system.

In the case of symmetrical diene, both possible and opposit electromeric changes occur, the diene would pass through an intermediate resonance structure with a distributed electronic charge, typical to the perturbed state.
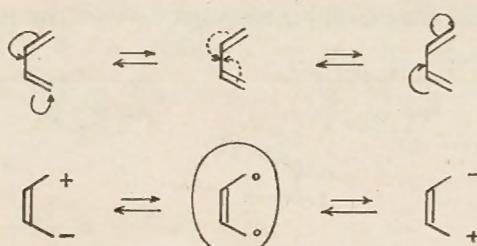

Fig. 3. — Acting resonance form.

• Indicate a single unshared electron.

Dotted arrows show the movement of single electrons.

The intermediate acting resonnance form provides each atom C_1-C_4 of the diene with a single unshared electron as follows :

$$\overset{\text{H}}{\underset{\overset{..}{\text{H}}}{\bullet \overset{..}{\text{C}}}} : \overset{}{\underset{\overset{..}{\text{H}}}{\text{C}}} :: \overset{}{\underset{\overset{..}{\text{H}}}{\text{C}}} : \overset{\text{H}}{\underset{\overset{..}{\text{H}}}{\overset{..}{\text{C}} \bullet}}$$
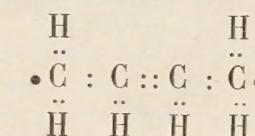
Now, dealing first with a symmetrical philodiene such as maleic anhydride, which is a typical example of a crossed or discordant polar conjugated system, we find, again, two possible and opposite ways of ionization under the influence of the activation promoting groups. As in the case of the diene, we can also assume that both activated forms have to pass through an acting resonance form with a distributed electronic charge.
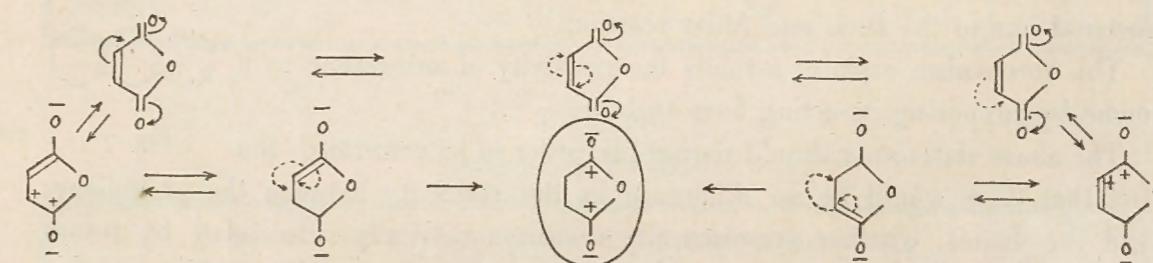
Fig. 4. — Acting resonance form.

This acting resonance form will suit undoubtedly that of the diene, since it provides again two single unshared electrons, which will be coupled together, in the easy formation of the newly formed, six-membered ring :
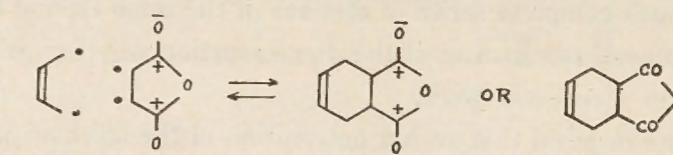
Fig. 5.

Such a reaction being reversible [32].

In the case of an unsymmetrical philodiene, such as the acroleine which is typical to the crotonoïd or the katioenoïd polar system, we have seen that the polarity of the

carbon atom C_1 is transferred to the carbon atom C_3 by the fact of conjugation :

$$CH_2 = CH - C = O \qquad \rightleftharpoons \qquad \overset{+}{C}H_2 - C = C \overset{H}{\underset{O}{\big\langle}}$$
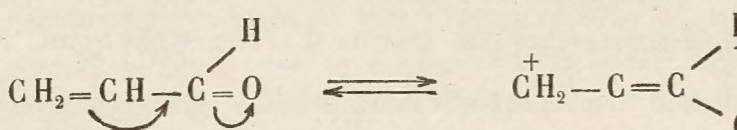
But here again we can assume that there is a resonance intermediate state as follows :
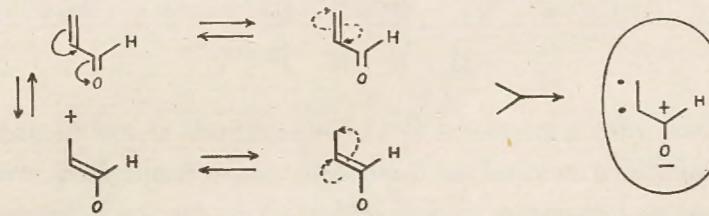

Fig. 6. Acting resonance form

This acting resonnance form provides each of the carbon atoms C_3, C_2 with a single unshared electron, and as a whole, this philodiene acts in the same way as the symmetrical one in the Diels and Alder reaction.

This mechanism explains actually the reactivity of anthracene as a diene by supposing its acting form to be :
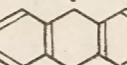

Fig. 7.

The above statements should require, in order to be confirmed, the fact that there would be no difference in the reactivity between the philodienes and the dienes, whether symmetrically or unsymmetrically substituted by resonnance promoting groups. If we design, for example, the philodiene by :

$$R_1 - CH = CH - R_2$$
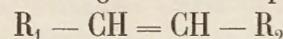
(R_1, R_2 being the promoting groups), there should be no difference in the reactivity in a series of compounds, where systematical changes are made in the substituents R_1, R_2 beginning with $R_1 = R_2$ and ending with $R_1 = H$ and $R_2 =$ a negative group.

Investigation of such complete series of olefines in the same type of reaction would shed light on the general mechanism of the diene reaction whether proceeding along different ways, or on a common path.

It should be borne in mind that such a description of the mechanism also accounts for these cases, where the activation of the diene is self-promoted, such as in the dimerization of isoprene to dipentene (which proves again to be reversible).

The result of a systematical study of condensations with dicyclohexenyl and $3.4.3'$ $4'$ Tetrahydro $1.1'$ binaphtyl (bis dialine) are summarized. Two groups of philodienic compounds are clearly discernible with equal and different substituents.

TABLE I.

ADDUCTS WITH DICYCLOHEXENYL.

PHILODIENE NAME	RATIO : $\dfrac{DIENE}{PHILODIENE}$	TEMPERATURE OF REACTION	YIELD	REFERENCE
Maleic anhydride.......	1 : 10	100°	95%	33
Trans-Dibenzoyl Ethylene	1.5 : 1	80°	85%	33
Trans-Cinnamic Acid....	1 : 1	180°	50%	33
Indene	1.5 : 1		43%	34
Trans-BenzalAcetoPhenone	1 : 1	180°	30%	33
Trans-Benzoly Acrylic Acid	1 : 1	80°	25%	33
Acroleine............	1 : 1	80°	20%	35

TABLE II.

ADDUCTS WITH BIS DIALINE.

PHILODIENE NAME	RATIO : $\dfrac{DIENE}{PHILODIENE}$	TEMPERATURE OF REACTION	YIELD	REFERENCE
Maleic anhydride.......	1 : 2	210°	87%	36
Maleic anhydride.......	1 : 10	100°	95%	33
Benzoquinone	1 : 10	150°	80%	33
Trans-Dibenzoylethylene..	1 : 1	200°	50%	33
α Naphtoquinone	1 : 2	130°	50%	33
Trans-Cinnamic Acid....				
Benzoyl acrylic acid.....				
Benzal Acetone	1 : 1	no reaction		
Benzal Acetophenone				

It is seen, however, that the yield vary with the changes in the ratio of components, solvents, etc. In many cases the drastic conditions cause side reactions, e. g. with Ketones and Quinones.

In view of the reversibility of the diene reaction, and in order to get a sound basis for comparison, it is necessary to use a large excess of one component. This, naturally, could only be the diene, which serves as solvent and diluent for the olefine. Dicyclohexenyl was chosen because of its excellent reactivity and its being a liquid of a high solvent power.

Results now obtained in 5 : 1 reaction mixtures are given in Table III.

TABLE III.

ADDUCTS WITH DICYCLOHEXENYL RATIO : $\frac{DIENE}{PHILODIENE}$ 5 : 1 .

PHILODIENE NAME	TEMPERATURE OF REACTION	YIELD	REFERENCE
Maleic Anhydride.	80°	95%	33.
Benzoquinone	80°	85%	33
α Naphthoquinone	100°	99%	33
Fumaric Acid	200°	80%	33
Trans-Benzalacetone	180°	76%	33
Trans-Dibenzalacetone	180°	95%	33
Trans-Cinnamic Acid.	180°	75%	33
β Nitrostyrene	80°	95%	38

It is obvious at once that no difference is detectable between symmetrical and unsymmetrical philodienes. Even the reaction temperature does not indicate any group difference; Furamic acid [37] which should behave like its cis-isomer, can be brought into reaction only at 200°. Whereas β Nitrostyrene reacts as easily as maleic anhydride at 80°.

If we add the recent observation of Joshel and Butz [24] that even ethylene undergoes the Diels and Alder reaction, when suitably activated, then we can safely conclude that our scheme represents satisfactorily the general reaction mechanism.

2. *The Stereoisomerism in the diene reaction.*—If we have to consider the maximum number of stereoisomers which would arise in the diene reaction between unsymmetrical dienes and philodienes, we can forecast, on a theoretical basis, the four asymmetrical carbon atoms of the newly formed ring to give :

$$n^2 = 4^2 = 16 \quad \text{Stereoisomers or 8 Racemates}$$
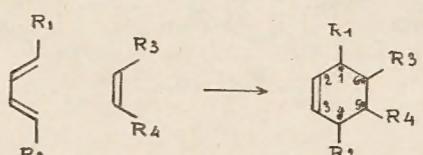
Fig. 8.

The isolation of more than two isomers in such a reaction, is so far unknown. Besides there is a very small evidence in the formation of stereoisomers in the other cases.

The first steps done in this field were those of Diels and Alder [39] when they described the endo-exo isomerization, occuring in the dimerization of cyclopentadiene :
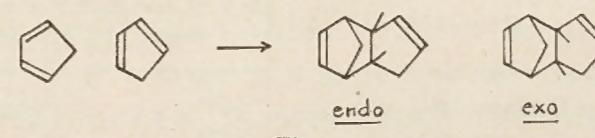

Fig. 9.

It is important to note that most of the adducts with cyclopentadiene and philodienes of the Katioenoid or crossed polar type such as :
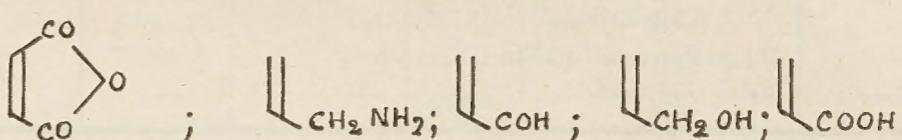
gave only the endo forms, apart from the single case of crotonaldehyde where an endo-exo (cis, trans) isomerization was suspected [40]. But, even then, no definite proof was given. Such a restriction providing a single sterical formation seems to be directed by the double bond of the newly formed six-membered ring; since in the case of the adduct formed with cyclopentadiene and fumaroyl chlorid it was possible

to obtain, partly, the endo anhydride, only after dehydrogenation of the adduct and distillation at high temperature of the free acid. The latter corresponded to the single endo adduct obtained, directly, with maleic anhydride and subsequent hydrogenation.


Fig. 10.
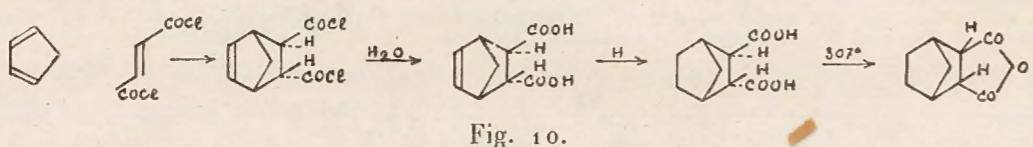
We give in Table IV the different isomers isolated in the reaction of dicyclohexenyl with some philodienic compounds. We shall try, on the light of the above described mechanism, to discuss the restrictions that rule this chemical change.

TABLE IV.

ISOMERIC ADDUCTS OF DICYCLOHEXENYL AND BIS DIALINE

DIENE	PHILODIENES	M. P. OF NORMAL ISOMER	M. P. OF SECOND ISOMER	REMARKS
Dicyclohexenyl.	Trans Cinnamic acid.........	$231°$	$282°$	
—	— Benzal acetone.........	$135°$		
—	— Benzal acetophenone....	$154°$	$216°$	
—	— Dibenzoyl ethylene	$162°$ or $182°$		isomorphic
—	— Benzoylacrylic acid	$259°$		form
—	— α Naphthoquinone......	$208°$		
—	— β Nitrostyrene.........	$187°$		
—	Dibenzalacetone (diadduct)....	$209°$		
Bis dialine....	Maleic anhydride...........	$256°$	$260°$	

b) *Preservation of the geometrical structure of the Philodiene.*—Dealing first with the philodiene compound, we find that its ethylenic bond forms the carbons 5 and 6 of the newly formed six-membered ring of the adduct. Carbon atoms 5 and 6 provide, of course, a cis-trans-isomerism of the group R_3, R_4 (see fig. 8).

It would be, however, impossible to realize such an isomerism, if we admit that the acting resonance form requires the symmetrical fission of the duplet a (or b) (see fig. 6) into two single unshared electrons. Because, in this case, although both

the tetrahedra could then rotate freely around the axle b (or a) there is only one single spatial arrangement which will fit the sharing of these electrons *in one plane* with those of the activated diene. This structure indeed is the one which preserves and maintains the original structure of the philodiene :
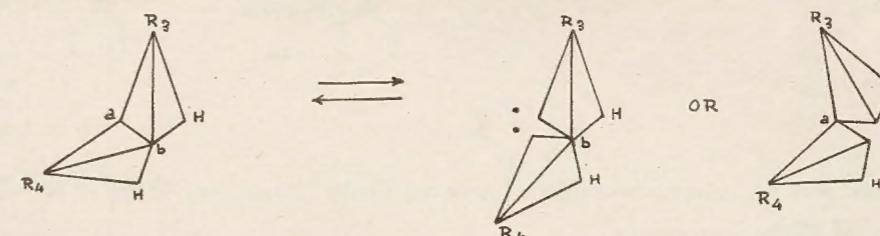

Fig. 11.

• indicates a single unshared electron.

The original cis structure is maintained in $(R_3\ b\ R_4)$ or $(R_3\ a\ R_4)$ provided that the single unshared electrons share in the same plane.

In order to confirm this statement, we chosed in our experiments the two isomers isolated by us from the interaction between dicyclohexenyl and trans-cinnamic acid. The original adduct, prepared first by Ch. Weizmann and Cow [41] and melting at $221°$, was found by us to consist of a mixture of two isomers melting at $231°$ and $281°$ respectively. Both adducts, when isolated in a pure state, were converted into their methyl esters by means of diazomethane, thus:
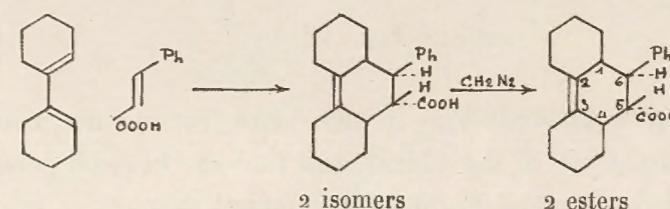

Fig. 12.

Two respective esters were obtained, melting respectively at $111°$ and $147°$.

In the mechanism described above, the phenyl and the carboxyl groups of the hydrogenated phenanthrene skeleton should be in a trans-position in both isomers. This is, indeed, the case, because, when hydrolized, in a butanolic solution of Sodium Butylate, both esters yielded respectively, on acidification, the original corresponding acids. Such a treatment [42] is known to preceed through the enol form of the

esters, thus destroying the assymmetry of carbon atom 5 (fig. 8), and regenerating on acidification, the more stable trans-form of the acids :
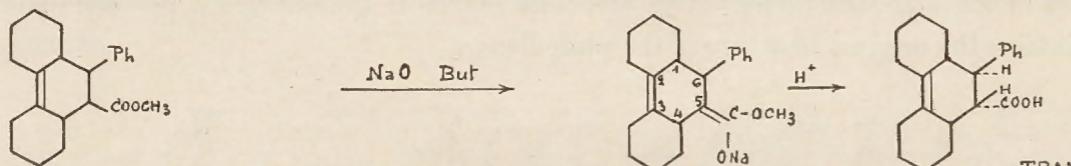

Fig. 13.

Since there was no interconversion of one acid into the other, there is no place for such a case of stereoisomerism.

On the other hand, one of the two isomeric cis adducts m.p. $256°$ prepared by us from the interaction between bis dialine and maleic anhydride, gave, on the same way, the corresponding cis di-ester m.p. $168°$ which was again converted by the same treatment to the more stable trans di-carboxylic acid melting at $239°$. The latter di-acid could not any more be dehydrated to its anhydride, owing to its stable trans structure (fig. 7).
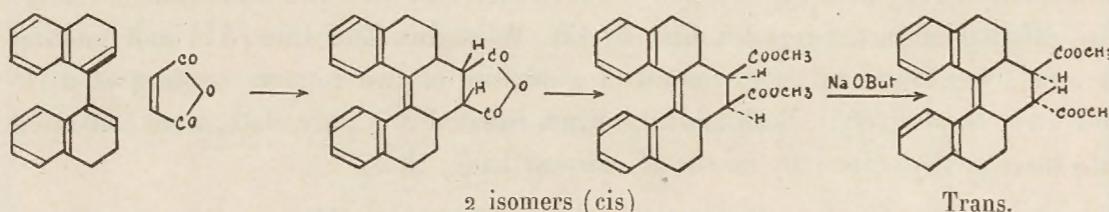

2 isomers (cis)   Trans.

Fig. 14.

Then one can safely conclude that in the diene reaction no cis-trans isomerism occurs in carbon atoms 5.6 of the adduct, and that the original geometric structure of the philodiene is maintained during this chemical change.

We shall now deal with the possible isomerism provided by the carbon atoms 1.4 (see fig. 8) of the newly formed ring.

Unlike the philodiene, there are two possibilities for the dienic compound to provide stereoisomerism in the carbon atoms 1.4. In fact, the resonnance acting form of the diene requires the fission of two pairs of shared electrons (in $C_1 C_2$ and $C_3 C_4$) from which a pair share again in $C_2 C_3$ of the conjugated system, while the other pair is equally distributed, in the form of two single unshared electrons in the carbon atoms C_1 and C_4 (fig. 3).

If we design, arbitrarily, by $a b, a' b'$ (see fig. 15) each two pairs of shared electrons, it is clear that such a fission could be symmetrical in $a a'$ or unsymmetrical in $a'b$ or ab', providing thus a cis-trans isomerism in the carbons 1.4 of the newly formed


Symmetrical fission   Unsymmetrical fission
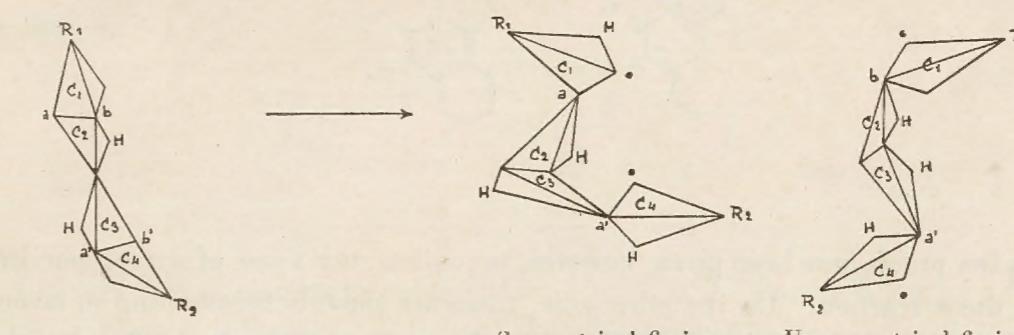
Fig. 15.

ring, since in every case the free unshared electrons of C_1 and C_4 of the butadienic compound have to be present in one plane when they share with those of the philodiene.

It is, however, noteworthy that when the conjugated system forms part a cyclic ring such as in the dicyclohexenyl, one of the covalencies usually occupied by H in $C_1 C_4$ becomes now engaged in the formation of the ring and the carbon atoms $C_1 C_2$ and $C_3 C_4$ lay in the same plane one another :
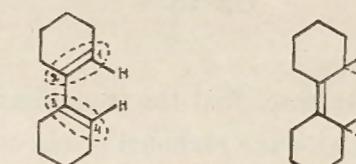

Fig. 16.

In such a case only a symmetrical fission, due to sterical reasons, is possible and this brings the remaining Hydrogen atoms of $C_1 C_4$ of the adduct in a cis position. Such a sterical preference seems to be directed by the double-bond in C_2-C_3, which tends to bring the hydrogenated phenanthrene skeleton in a monoplanar position. In fact, Adams and Geissman [43] showed, in 1935, that a cis position, in $C_1 C_4$, is greatly favoured in the adduct of 1.4 dimethyl butadiene and trans-dibenzoylethylene.

If such cases are eliminated, the only two remaining possibilities of Stereoisomerism,

out of the theoretical eight ones, would be those involved by the relative positions of the substituents in C_1-C_6 or in C_4-C_5 :
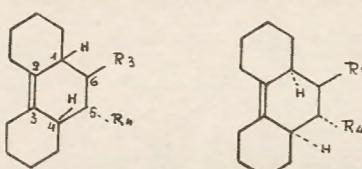

Fig. 17.

Very few proofs have been given, however, to confirm such a case of stereoisomerism in the diene reaction. On the other side, there are some facts militating in favour of the presence of simple *isomers*, differing by the position of the double bond of the newly formed ring.

Farmer and Warens [44] were the first, in 1929, to ascribe such a shift in their adduct with sorbic acid and maleic anhydride :
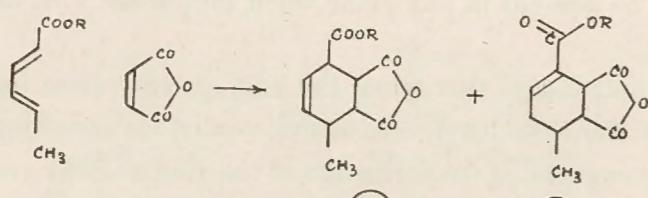

Fig. 18.

Such a suggestion was, on the base, that the isomerism was favoured in B by the conjugation of the double bond with the carbonyl group of the carboxyl. This hypothesis was met by Diels and Alder [45] with a great controversy. In our opinion, however, it seems that such an isomerism is much in favour. Besides, it was known that in the case of cyclohexenyl cyclohexanone [46], two isomers were formed, thus :
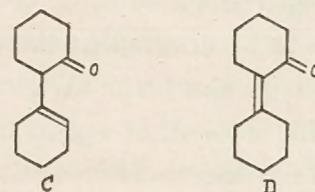

Fig. 19.

Where the form C is more stable, although it requires the destruction of the conjugation in D. Moreover, the presence of two isomeric adducts in the reaction between 2.3 dimethyl butadiene and trans-benzoyl-acrylic acid, reported by Fieser and Fieser [47], in 1935, could by no means be explained as *stereoisomers* as stated by them :
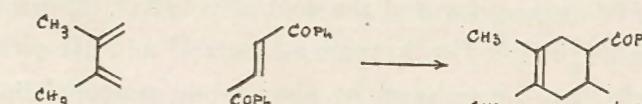

Fig. 20.

The only way of isomerism being indeed a shift of the double bond.

In our cases of isomerism, we suggest the main product to be that of the normal C_2-C_3 double bond, since it is known to be very unreactive towards bromination and catalytic hydrogenation, while the second isomer should contain the double bond in C_3-C_4 (fig. 21 a); or in C_1-C_6 or C_4-C_5 (fig. 21 b). Shifts in C_1-C_6 or C_4-C_5 seem to be less likely to occur than in C_1-C_2 or in C_3-C_4 since they are extra nuclear (or exocyclic), although a conjugation with the radicals R_3 R_4 might facilitate such shifts. At last we must admit that in the case of bis diadduct, new cases of stereoisomerism are obviously expected as well as in the cases of substituted fulvenes [48].
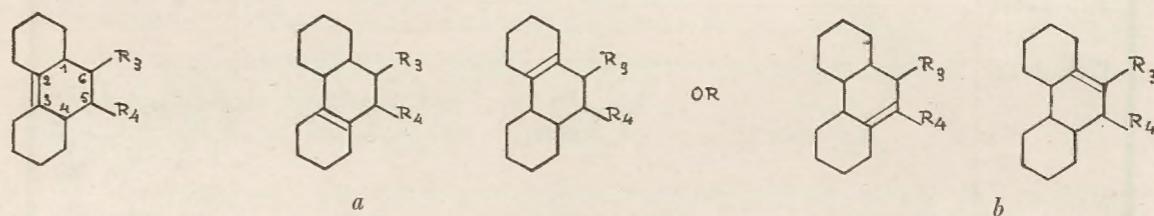

Fig. 21.

3) *Chemical behaviour of the adducts.*—It is noteworthy to report some of the chemical behaviours of dicyclohexenyl adducts. In most cases, the isomer formed is present in a very small proportion (usually less than 10 %). Therefore, the reactions leading to its isolation and determination of its structure are very difficult to be brought to an end. Besides, the adducts are usually characterized by their resistance to various reagents.
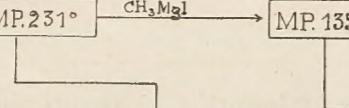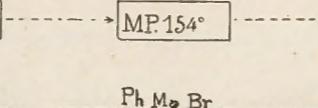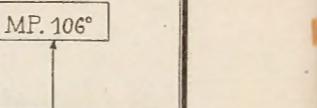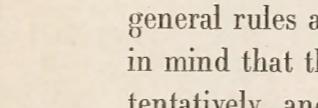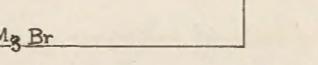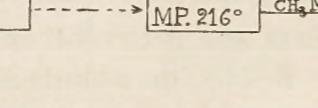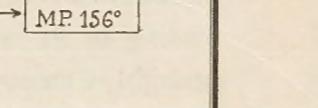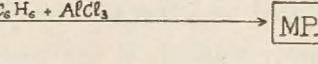
In the adduct of dicyclohexenyl and trans-cinnamic acid, the high melting isomer m.p. 281° is sometimes entirely missed, if the reaction is not carried in a closed vessel. On the other hand, the amount of the main isomer m.p. 231° is by no means

affected by such a change. In Table V we tried to connect the different isomeric adducts provided by Dicyclohexenyl. The methyl esters of the cinnamic acid adducts I_A I_B were recovered unchanged after 6 hours boiling with Sodium-ethylate, but were readily saponified to give the corresponding acids after one hour boiling with Sodium butylate. In this way, it could be shown that the adduct with ethyl cinnamate m.p. 85° derives from the lower melting form of the acid m.p. 231°. Such a hydrolysis was regarded as impossible [49]. The Ketonic adducts II and III yielded no carbonyl derivatives, nor could they be reduced by aluminium isopropylate. None of these adducts reacted with Grignard reagents under the normal conditions (a boiling mixture of Ether and benzene).

The ester of I_A, m.p. 111° was converted into II_A by means of $CH_3 MgI$. in boiling toluene, but was not attacked by $Ph. Mg. Br.$, so that *the isomeric forms of I_A and III_A could not be linked together*. The ester I_B, m.p. 147° was recovered unreacted under the same conditions.

TABLE V.

STRUCTURAL RELATION BETWEEN ISOMERIC ADDUCTS OF DICYCLOHEXENYL.

Adduct II_A, however, could be converted into the dimethyl substitued carbinol by means of $CH_3 MgI$. Hence, we tried to link II_A with III_A by permitting the former to react with $Ph.Mg.Br.$ and the latter with $CH_3 Mg. I$; II_B gave IV_A, while III_A gave no definite product; contrarily, its high melting isomer III_B gave under the same condition IV_B. (The methylenic structure of IV is to be preferred according to the very strong absorption of Bromine, which proves, at the same time, that no cyclization has occured). At last, we tried to connect directly I_A with III_A by treating I_A with Aluminium Chloride in benzene solution, but the isolated Ketone III_C of the Friedel and Crafts reaction, differed from either III_A or III_B and was supposed to have suffered an isomeric change, under the influence of the catalyst.

Table V shows the structural relations between the different adducts of Dicyclohexenyl. A full arrow shows the interconversion of one adduct to another with the same structural formula; a dotted arrow shows such a possible interconversion which was not yet established experimentally. Isomers A, the lower melting ones, are arbitrarily supposed to be the normal ones with the C_2-C_3 (fig. 8) double bond, while isomers B, the higher melting ones, are supposed to have suffered a shift of the double bond in the any four possible positions of the medium ring. This distinction is, however, very arbitrary, since in the case of the adduct III, the III_B isomer was the main product of the reaction and as such should have been considered as the normal one.

No definite conclusion can, of course, be drawn from these negative results, but there remain some facts which enable us to restrict certain theoretical possibilities of reaction, in the diene synthesis.

4) *Conclusion.*—All the experimental facts discussed above, lead to the following general rules about the sterical course of the diene reaction, but it should be borne in mind that the first one has been really proved, whereas the others are formulated tentatively, and have to await further investigations to be settled definitely :

a) The structure of the philodienic component is preserved unchanged in the adduct. No cis-transisomerization occurs.

b) No isomerism is caused by different spatial arrangements at carbon atoms C_1, C_4 of the newly formed ring. The cis arrangement is the most probable structure.

c) There is small evidence of stereoisomerism caused by the relative arrangement of the substituents at carbon atoms C_1-C_6 or C_4-C_5.

d) Isomeric adducts differ in the position of the double bond of the newly formed six-membered ring.

5

EXPERIMENTAL PART (A).

1) *1-(o-chlorophenyl) 2-phenyl naphthalene IX.*—To a Grignard solution prepared from o-chloroiodobenzene (12 g) and magnesium (1.2 g) an ethereal solution of 2-phenyltetralone [15] (4 g) was added and the mixture refluxed for 12 hours. From the reaction product, a high boiling fraction, b.p. 170-185°/0.05 mm. was isolated yield 5.5 gr. This syrup could not be induced to crystallize. Dehydration was effected by KHSO₄ at 150-160°. The dehydronaphthalene derivative (VIII) crystallized directly on trituration with methanol. From petrolum-ether (80°), crossed prismatic rods mp. 129-130°. Yield : 2.5 g.

$$\text{Anal. Calc'd for } C_{22} H_{17} Cl : C\ 83.5 : H,\ 5.4$$
$$C\ 82.8 : H,\ 5.3$$

VIII was recovered unchanged when heated with molten KOH at 230° or when treated with a mixture of $AlCl_3$-NaCl (4 : 1) at 140°.

Dehydrogenation was effected by heating VIII with Selenium to 260° for 10 hours. The reaction mixture was extracted with ether, which left a thick sirupy mass crystallizing with a few drops of methanol. From glacial acetic acid, blocs : mp. 112-113° (IX) :

$$\text{Anal. Calc'd for } C_{22} H_{15} Cl : C\ 84.1 : H\ 4.8$$
$$C\ 83.7 : H\ 4.8$$

The picrate was prepared in ethanolic solution and crystallized from isopropanol in needles m.p.-120-122°.

$$\text{Anal. Calc'd for } C_{23} H_{18} O_7 N_3 Cl : C\ 61.9; H\ 3.3; N\ 7.7$$
$$\text{Found : } \qquad\qquad C\ 61.8; H\ 3.8; N\ 7.8.$$

2) *9-Spiro cyclohexane, 3-4 benzofluorene XII.*—To a Grignard solution, prepared from α-bromonaphthalene (0.1 mol) and magnesium (0.1 mol), cyclohexenyl cyclohexanone (0.1 mol) in benzene was added, the mixture refluxed for 4 hours and

worked up as usual. Distillation yielded 13 gr. (42 %) of a fraction b. p. 225-230° (0.8 m/m) (X).

$$\text{Anal. Calc'd for } C_{22} H_{26} O; C\ 86.2 : H\ 8.5.$$
$$\text{Found : } \qquad\qquad C\ 85.6 : H\ 8.2.$$

For cyclization of X, benzene proved the most suitable. 12 g. of the carbinol X in benzene were added dropwise to a suspension of $AlCl_3$ (15 g.) in benzene at 0° The colour turned quickly to red-violet. It was left for 6 hours at 0° then 12 hours at room temperature. $AlCl_3$ passed into solution and two layers were formed. The reaction product was divided into 3 fractions by distillation.

a) b.p. 200-230° (0.1 m/m). Thick yellow oil, 4.5 g. Its picrate was prepared in isopropanolic solution and crystallized from glacial acetic acid as fine brown needles m.p. 160-161° (XI_b?).

b) b.p. 230-240° (0.1 m/m). This fraction (4 g.) proved to be a mixture of (a) and (c), because its picrate consisted of a mixture of the two picrates isolated in pure condition.

c) b.p. 250-270° (0.1 m/m) yellow reddish oil (1.5 g.). The picrate was prepared as described under (a) and formed golden rods m.p. 169-170° (from glacial acetic acid) (XI_A?).

$$\text{Anal. Calc'd for } C_{28} H_{27} O_7 N_3; C\ 65 \quad ; H\ 5.2; N\ 8.1$$
$$\text{Found m.p. } 160°\text{-}1° \qquad C\ 64.9; H\ 5.2; N\ 8.-$$
$$\text{m.p. } 169\text{-}70° \qquad C\ 65.3; H\ 5.1; N\ 8.2$$

Dehydrogenation was best obtained with fraction (C), whereas the other fractions gave poorer yields. 15 g. of (c) and 25 g. of Selenium were heated to 320° for 30 hours. The hot mixture was then stirred carefully into petroleum-ether (80°) and the product washed with Na OH and distilled. The main fraction b.p. 220-240° (0.1 m/m) consisted of a reddish oil with green fluorescence (9.5 g.). This product (XII) was purified via its picrate, which was prepared in glacial acetic acid with addition of a little petroleum-ether in order to get a homogeneous solution. The picrate crystallizes from glacial acetic acid in red rods m.p. 141-142° 7 g. of the crude hydrocarbon yielded 8 g. of picrate.

$$\text{Anal. Calc'd for } C_{28} H_{23} O_7 N_3 (XII)\ C\ 65.5; H.\ 4.45; N\ 8.2$$
$$\text{Found} \qquad\qquad C\ 65.8; H.\ 4.2\ ; N\ 8.-$$

5 g. of the picrate yielded 2.5 g. of the Spirane XII b.p. 225-230° (0.05 m.) as a thick yellow oil with strong green fluorescence. It dissolves readily in petroleum ether or acetone but not in acetic acid. With conc. Sulphuric acid a pink coloured solution is obtained on gently heating which turns slowly to green.

Anal. Calc'd for $C_{22} H_{20}$: C 93; H 7.
Found   C 93.4; H 6.7.

Oxidation of XII to XIII : 0.25 g. of the foregoing hydrocarbon in acetic acid (5 cc.) were boiled with $K_2 Cr_2 O_7$ (0.5 g.) for 5' the quinone precipitated on addition of water. It was recrystallized twice from high boiling petroleum ether and formed beautiful long red plates m.p. 228° (XIII). The quinone dissolves in conc. Sulphuric acid with cherry red colour.

Anal. Calc'd for $C_{22} H_8 O_2$: C 84.1 ; H 5.7.
Found   C 84.- ; H 5.8

3) *Tetrabenz-Naphthalene* (*XV*).—The Grignard reaction between 9-bromophenan-threne (26 g.), magnesium (2.5 g.) and cyclohexenyl cyclohexanone (18 g.) in ben-zene, gave after 10 hours boiling a mixture which after decomposition and distil-lation yielded 17 g. of a bright yellow syrup. b.p. 270-290° (0.1 m/m) cyclization of this carbinol (16 g.) was carried out as described above, with $AlCl_3$ in benzene solution and gave as the main product a fraction b.p. 320-360° (0.1 m/m). Yield : 10 g. which was used directly for dehydrogenation.

10 g. of cyclization product and selenium (12 g.) were heated to 350° for 20 hours, the mass extracted with hot CCl_4, washed with NaOH, and fractionnated.

a) b.p. 230-260° (0.2 m/m); reddish oil, 3 g. In acetic acid solution, a plastic picrate was formed. The solvent was decanted and the product kneaded in a mortar with petroleum ether. Thereafter, it could be recrystallized from isopropanol brown leaflets m.p. 157-159°. (*This points to the Spirane derivative.*)

Anal. Calc'd for $C_{32} H_{25} O_7 N_3$: C 68.2; H 4.4.
Found   C 68.- ; H 4.0

b) b.p. 290-320° (0.1 m/m). Dark red resin; 1.5 g. Here again, the picrate which was prepared in acetic acid solution, first formed a black plastic mass, and

acquired granular consistency only after trituration with butyl acetate and petroleum ether. Yield : 1.8. It was dissolved in isopropanol (50 cc.) and nitrobenzene (2 cc.) by prolonged boiling and then crystallized in red black rods [16] m.p. 210-212° (XV). This procedure had to be repeated 2-3 times.

Anal. Calc'd for $C_{32} H_{19} O_7 N_3$: C 68.9; H 3.4; N 7.5.
Found   C 68.6; H 3.2; H 7.4.

4) *6-Acetyl Chrysene*.—After many trials the best method found was the following : In a three necked flask, fitted with an efficient stirrer and reflux condenser, are mixed chrysene (40 g.) and acetyl chloride (75 cc.) with carbon disulfide (500 cc.). Alu-minium chloride (35 g.) is added at room temperature within five minutes. Stirring is continued for eight hours at room temperature then with a slow gradual heating to 60° within six hours. The solvent is now distilled off and the residue decomposed with ice-cold hydrochloric acid. Traces of solvent are removed by steam distillation, and the remaining black syrup is poured while hot in a mortar. On cooling it soli-difies and is then pounded in small particles and dried in a water bath. The dry powder is extracted two to three times with boiling benzene and the solution distilled in vacuo. b.p. 251° (0.1 m/m). The distillate solidifies on trituration with me-thanol. Recrystallization from petroleum ether gave yellowish rods m.p. 145°. Yield 35 g. The black residue of the extraction, is now treated several times with boiling xylene and the solution again distilled in vacuo. After a small head of 6 acetyl chrysene, two fraction could be isolated.

a) b.p. 255-260° (0.05 m/m) from glacial acetic acid, needles m.p. 254° (this is supposed to be the 2 acetyl chrysene) with conc. Sulphuric acid, cherry red colour.

Anal. Calc'd for $C_{20} H_{14} O$: C 88.9; H 5.2.
Found   C 88.8; H 5.1.

b) b.p. 270-280° (0.05 m/m). From much butanol, microcrystalline needles m.p. 296°. (This is the diacetyl chrysene).

Anal. Calc'd for $C_{22} H_{16} O_2$: C 84.6; H 5.1.
Found   C 84.3; H 5.5.

5) *Grignard reactions*.—These were carried out with three equivalents of the ma-gnesium compound and the second component (6 acetyl chrysene) added either as

powder or suspended in xylene. The ether was then removed and the xylene solution boiled for four hours.

A) With methyl magnesium iodide. On decomposition of the reaction mixture from 14 g. of 6-acetyl chrysene a white precipitate settled down immediately from the xylene solution. It is *carefully* washed free from *traces* of acid and recrystallized from petroleum ether (130°). (The solution has usually a faintly violet colour.) Rods m.p. 172° (XVI) with conc. $H_2 SO_4$ deep violet colour. Yield 9 gr. = 60 %.

Anal. Calc'd for $C_{21} H_{18} O$: C 88.1 ; H 6.3
Found C 87.8 ; H 6.4

On preparation of the picrate of XVI, dehydration occurs, so that the product is identical with that of the diene XVII. Red needles (from acetic acid) [17] m.p. 144°.

Anal. Calc'd for $C_{21} H_{19} O_7 N_3$: N 8.5
Found : N 8.9

The content of the xylene solution was distilled in vacuo b.p. 220° (2 m/m), white plates (from glacial acetic acid) m.p. 161° (XVII). Yield 3.5 g. = 25 %.

Anal. Calc'd for $C_{21} H_{16}$: C 94.- ; H 6-.
Found : C 94.2 ; H 5.9.

The same diene was obtained in quantitative yield from the carbinol XVI in a cooled acetic acid solution, when cold $H_2 SO_4$ conc. was added dropwise. The sparingly soluble diene XVII separates almost immediately from the acetic acid solution. If the reaction is, however, carried out above 100°, and also in numerous other experiments with the diene XVII (e. g. in boiling its solution in $Sn Cl_4$) a high melting dimer (?) was obtained. It was recrystallized from ethyl benzoate-acetic anhydride mixture or from nitrobenzene m.p. 307°.

Anal. Calc'd for $C_{21} H_{16}$: C 94.- ; H 6.
Found : C 93.7 ; H 6.3.-

The isomeric acetyl chrysene, of m.p. 254° (2 acetyl chrysene ?) yielded in the same way an isopropenyl compound. m.p. 288° (leaflets, from glacial acetic acid).

Anal. Calc'd for $C_{21} H_{16}$: C 94.- ; H 6.-
Found : C 94.3 ; H 6.-

B) With ethyl magnesium bromide : The reaction yielded 26 % of the carbinol m.p. 119° (rods from petrol ether (130°); and 68 % of the diene XXIII R = CH_3 m.p. 159-160° (leaflets from acetic acid). The carbinol was dehydrated quantitatively by the method just described. Both compounds were found to be inert towards maleic anhydride and to yield the same picrate m.p. 132-133°. (Red needles from acetic acid).

Anal. *A*) of the carbinol Calc'd. for $C_{22} H_{20} O$: C 88 ; H 6.7. Found : C 87.8 ; H 6.5.
B) of the diene Calc'd. for $C_{22} H_{18}$: C, 93.6 ; H, 6.4. Found : C, 93.3 ; H, 6.3.
C) of the picrate Calc'd. for $C_{28} H_{21} O_7 N_3$: N, 8.2. Found : N, 8.5.

c) With n. propylmagnesium bromide : In this case, only the diene was obtained. Yellow oil b.p. 210-215° (0.1 m/m). Yield : 67 %. After some months microcrystalline needles appeared XXIII R = $C_2 H_5$ m.p. 102° (from ethanol). The picrate crystallized in red needles from glacial acetic acid m.p. 138/140°.

Diene Anal. Calc'd. for $C_{23} H_{20}$: C 93.2 ; H, 6-8. Found : C 93.2 ; H 6.6.
Picrate — — $C_{29} H_{23} O_7 N_3$: N 8. Found : N 8.3.

d) With n-butyl magnesium bromide : Only the diene is obtained. Yellow oil, b.p. 230-235° (0.1 m/m). After six months, it crystallized partially, but the solid had a low m.p. (about 40°) and could not be purified in crystalline state. Its picrate melted at 129-130°.

Diene Anal. Calc'd for $C_{24} H_{22}$: C 92.9 ; H, 7.1. Found : C 93.1 ; H, 7.
Picrate — — $C_{30} H_{25} O_7 N_3$: N 7.8. Found : N 8.2.

6) *Catalytic reductions.*—*a*) of XVII. 6 Isopropenyl chrysene (2.7 g.) in ethyl acetate (150 cc.) in the presence of P*d*-B*a* SO_4 catalyst absorbed 220 cc. H_2 at room temperature in three hours. (Calc'd. 220 cc.). The 6 Iso-propylchrysene, V, R = H was directly recrystallized from petrol-ether (130°). Needles m.p. 137°. Yield 2.4 g. Its picrate gave needles from acetic acid m.p. 144/145°.

Anal. Calc'd for $C_{21} H_{18}$: C 93.3 ; H 6.7. Found : C 93.1 ; H 6.5.
Picrate : Anal. Calc'd for $C_{27} H_{21} O_7 N_3$: N 8.3. Found : N 8.7.

b) of XXIII R = CH$_3$: 1.6 g. of this hydrocarbon absorbed the required amount of H$_2$ only after 24 hours. From petrol-ether (80°) sharp plates m.p. 100°. Its picrate gave beautiful red slender needles, from acetic acid m.p. 133°.

Hydrocarbon Anal. Calc'd for C$_{22}$ H$_{20}$; C 93 ; H, 7. Found : C 93.1 ; H 6.8
Picrate — — C$_{28}$ H$_{23}$ O$_7$ N$_3$; N 8.2. Found : N 8.45.

Neither of the two higher homologs of XXIII R = C$_2$ H$_5$, R = C$_3$ H$_7$ could be reduced at room temperature or at 80°.

7) *Condensation with maleic anhydride*.—Carefully crystallized dimethyl—6 chrysenyl carbinol XVI (or the diene XVII) (8.5 g.) free from traces of mineral acid, was boiled for two hours with maleic anhydride (17 g.) (5 eqv.) in acetic anhydride (30 cc.). On cooling 9 g. of the adduct XVIII were obtained. The mother liquors yield an additional crop of 1 g. by cautious addition of water. Recrystallization from acetic acid yielded either prismatic blocs (from concetrated solutions) or white needles (from dilute solutions) m.p. and mixed m.p. 262°.

Anal. Calc'd for C$_{25}$ H$_{18}$ O$_3$; C 82- ; H 4.9.
Found : C 82.4 ; H 5-.

8) *Aromatization of the adduct*.—A hot solution of VIII (5 g.) in acetic anhydride (100 cc.) was added to a hot solution of lead tetraacetate (17 g.) in acetic acid (100 cc) and the mixture boiled for two hours. On cooling, yellow rods were deposited m.p. 325° (from ethyl benzoate) XIX yield 1.5 g. = 20 %.

Anal. Calc'd for C$_{25}$ H$_{14}$ O$_3$: C 82.9 ; H 3.9.
Found : C 83- ; H 3.9.-

When the dehydrogenation was tried with bromine in acetic acid solution in presence of Sodium acetate [18] XIX was obtained in about 30 % yield but a form which could not be satisfactorily purified from contaminations.

9) *Decarboxylation*.—*a*) When the adduct XVIII (1.2 g.) was heated with zinc dust (0.5 g. in a low vacuum (100 m/m) a yellow liquid distilled off at 280-300°. Which proved to be the diene XVII m.p. 160°.

b) XVIII (5 g.) and Selenium (2.5 g.) were heated slowly to 270-310° (bath temperature), during 4 hours a small amount of crystalline material 150 mg. sublimed at normal pressure. The reaction mixture extracted with ethyl acetate, and the extracted material distilled at b.p. cc. 250° (0.5 m/m). 2.2 g. of a yellow syrup were obtained which solidified on treatment with acetone isopropanol. From isopropanol yellowish rods m.p. 139° XXI which were identical with the sublimed portion. The picrate gave red rods from acetic acid m.p. 140°.

Hydrocarbon Anal. Calc'd for C$_{23}$ H$_{20}$: C 93.2 ; H 6.8.
Found : C 93.1 ; H 6.8.

Picrate — — C$_{29}$ H$_{23}$ O$_7$ N$_3$: N 8.
Found : N 8.55.

The hydrocarbon XXI (50 mgr.) was oxidized with potassium dichromate (60 mgr.) in acetic acid (2 cc.) by boiling for 10'. The quinone was precipitated by water, then treated with ethanol and recrystallized from high boiling petrol ether. Short red rods, m.p. 178° (XXII) :

Anal. Calc'd for C$_{23}$ H$_{18}$ C$_2$: C 84.7 ; H 5.5.
Found : C 84.4 ; H 5.7.

When the hydrocarbon XXI (0.8 g.) was heated with selenium (0.4 g.) to 310-320° for 12 hours, and the mass extracted with boiling xylene, an oil b.p. 260-265° (0.02 m/m) was obtained, which in recrystallization from isopropanol yielded yellowish rods, m.p. 137-138°, identical with the starting material and a minute amount of small blocs which adhered to the walls. This second substance was separated and yielded from an acetic solution a picrate (red rods) m.p. 165°. Its amount, however, was not sufficient for analysis.

10) *Decarboxylation of XIX with copper*.—5 g. of XIX and bazic copper carbonate (5 g.) were heated in quinoline (35 cc.) for half an hour. Then benzene (100 cc.) was added and the solution washed with an excess of dilute sulphuric acid. On concentrating the benzene solution, a small amount of crystals separated. From butyl acetate, beautiful prisms m.p. 292-293° (XX *a* or *b*).

Anal Calc'd for : C$_{24}$ H$_{16}$ O$_2$: C 85.7 ; H 4.8.
Found : C 85.4 ; H 5.1.

EXPERIMENTAL PART (B).

I. REACTIONS WITH DICYCLOHEXENYL.

1) WITH TRANS-CINNAMIC ACID.—1. 2. 3. 4. 5. 6. 7. 8. 9. 10. 11. 14 Dodeca-hydrophenanthrene—9 phenyl—10 Carboxylic Acid.—The reaction between dicy-clohexenyl (12 g.) and Cinnamic Acid (11 g.) is carried out in a sealed tube at 180° for 8 hours, and the reaction mass triturated with cold methanol. The crude product
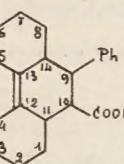
(17 g.) is extracted twice with 60 cc. boiling ethanol. The ethanolic solution de-posits the main product (about 10 g.) in form of needles m.p. 231°, it is recrystallized from high boiling petroleum ether. The residue of the alcoholic extraction (about 1 g.) was dissolved in 60 cc. of boiling butanol from which the second isomer was obtained as long prisms m.p. 281°-282°.

Anal. Calcd for : $C_{21} H_{26} O_2$: $C = 81.3$; $H = 8.4$.
Found : $C = 81.1$; $H = 8.1$.

The acid m.p. 231° was neither decarboxylated by basic copper carbonate, in boiling quinoline, nor by heating it with soda lime at 350°.

The methyl ester of the adduct m.p. 231° was prepared by means of diazomethane. Recrystallization, from methanol, yielded white needles, m.p. 111-112°.

Anal. Calcd. for $C_{22} H_{28} O_2$: $C = 81.5$; $H = 8.6$; $OCH_3 = 9.6$
Found : $C = 81.2$; $H = 8.2$; $OCH_3 = 9.8$

The ester was neither attacked by alcoholic sodium hydroxide solution, nor by sodium ethylate. Sodium butylate, in boiling butanol, however, produced the sodium salt of the original acid, which crystallized on standing over night. The precipitate was filtered off, acidified, and the resulting acid recrystallized from ethanol. M.p. and mixed m.p. 231°.

The same result was obtained by saponification of the ethyl ester m.p. 85°, which was prepared directly by condensation of dicyclohexenyl with ethyl cinnamate and was reported to resist normal saponification methods extraordinarily [49].

The acid, m.p. 282°, reacted much slowlier with diazomethane than its isomer. From petroleum ether, the ester was obtained as short needles m.p. 147°.

Anal. Calcd. for $C_{22} H_{28} O_2$: $OCH_3 = 9.6$ %.
Found : $OCH_3 = 9.6$ %.

The ester was again saponified with sodium butylate in 4 hours, as described above, and yielded the original acid m.p. 282°.

Variations of the condensation reaction with cinnamic acid.— *a*) Dicyclohexenyl (20 g.) and cinnamic acid (18 g.) were heated together in an open vessel at 175° for eight hours. The isomer, m.p. 231° was obtained exclusively. Yield 15 g. = 40 %.

b) The same amounts were heated together at 205-210° for 6 hours. Again, no trace of the isomer m.p. 282° was detected. Yield of m.p. 231° 18 g. = 47 %.

c) When 3 g. of the isomer m.p. 231° were heated in a sealed tube at 200° for 5 hours, no isomerization occured.

d) When 3 g. of the same acid were heated in a sealed tube to 250° for one hour, no trace of the second isomer was detectable.

2) WITH BENZAL ACETONE.—9. *Phenyl*-10 *acetyl, dodecahydrophenanthrene.*—Dicycloh-exenyl (10 g.) and benzalacetone (12 g.) were heated together for 3 hours at 175°. The reaction was interrupted because of the occurrence of drops of water, which indicated the onset of selfcondensation of the ketone. By fractionated distillation 5 g. of a fraction, b.p. 180-190°/0.5 mm., were obtained, which crystallized on trituration with methanol. An ethanolic solution of this material deposits .clusters of needles. M.p. 135°. Yield 27 %.

Anal. Calcd. for $C_{22} H_{28} O$: $C = 85.7$; $H = 9.1$.
Found : $C = 85.7$; $H = 8.9$.

The same results were obtained in a sealed tube and in an open flask. The head of the distillation (16 g.) which passes over at 120°/2.5 mm. represents the starting mixture. It was again heated under the same conditions, as described above, and yielded a further crop of 2 g. of the adduct. It is not advisable to continue by the same method because of the increase in self-condensation products of the ketone. The adduct gave no hydrazone or semicarbazone and was not reduced by aluminium isopropylate, even in boiling xylene.

3) WITH TRANS-BENZALACETOPHENONE. —9. Phenyl-10 benzoyl-dodecahydrophenanthrene.— Dicyclohexenyl (9 g.) and benzalacetophenone (11 g.) were heated together in an open vessel at 180-185° for 6 hours. The reaction mixture crystallized partially with ethanol, yielding 7 g. of the isomer m.p. 216°. After filtration, it is necessary to wash with petroleum ether, which removes the second isomer m.p. 154°. Recrystallization from petroleum ether (130°) gave needles m.p. 216°. Yield 6 g.

Anal. Calcd. for $C_{27} H_{30} O$: $C = 87.6$; $H = 8.1$.
Found (m.p. 216°) : $C = 87.6$; $H = 8.3$.
(m.p. 154°) : $C = 87.2$; $H = 8.2$.

The mother liquors of the alcohol, petroleum-ether, were distilled in vacuo at 220-240°/0.4 mm. A fraction was obtained, which was hardly induced to crystallization by treatment with methanol. From isopropanol needles m.p. 153/154°. Yield : 1 g. The material, which is easily soluble in petrol ether, gives no ketone derivative like its isomer.

4) WITH TRANS-DIBENZOYLETHYLENE. —9. 10 Dibenzoyl-dodecahydrophenanthrene.— a) Dicyclohexenyl (2.5 g.) trans-dibenzoylethylene (2.5 g.) in xylene (15 cc.) were boiled for 3 hours, and the solution left overnight in an ice-box. A small amount of crystals was deposited showing m.p. 162°. To the filtrate an equal volume of ligroine was added to precipitate a reddish yellow material. This was recrystallized from petroleum ether (130°) or butanol and formed brownish blocs m.p. 182°. Yield 2 g. The substance dissolves in cold sulphuric acid with brown colour.

Anal. Calcd. $C_{28} H_{30} O_2$: $C = 84.4$; $H = 7.5$.
Found : $C = 84.3$; $H = 7.6$.

The first crystallizate m.p. 162° when recrystallized from the same solvent, gave a mixture of white plates and yellow-brown prisms. These were separated mechanically. The prisms were identical to the product m.p. 182° whereas the plates were recrystallized several times from petroleum ether. After each recrystallization, the mixture of crystals was separated. However, the product m.p. 182° appeared again and again, whereas, the product m.p. 162° disappeared gradually.

b) 1 g. of dicyclohexenyl and 1 g. of the philodiene in ethanol (10 cc.) were boiled for 6 hours. Several crops of crystals were collected on gradual cooling, all of them proved to be the pure substance m.p. 182°. Yield 1.45 g. = 85 %. No trace of m.p. 162° was detected.

c) Dicyclohexenyl (3.3 g.) dibenzoylethylene (4.7 g.) in notrobenzene (30 cc.) were heated at 150° for one hour, to 175° for one more hour, and finally boiled for 10 minutes. The solvent was removed by steam, and the residue treated with alcohol. After repeated recrystallizations from butanol (with addition of charcoal) we obtained 5.5 g. of the material m.p. 182°.

Reactions with the above adduct.—a) The adduct (1.6 g.) was dissolved in boiling acetic anhydride (25 cc.) and 5 drops of sirupy phosphoric acid (d = 1.75) were added. The colour changed immediately to red-brown. After 10 minutes the solution was cooled and deposited a crystalline mass, which was recrystallized from butanol. The solution shows intense green fluorescence and deposits yellow rods m.p. 179-180°. Yield 1.4 g. (Fluorescence is observed in solvents, containing oxygen or halogen but not in hydrocarbons).

Anal. Calcd. for $C_{28} H_{28} O$: $C = 88.4$; $H = 7.4$.
Found : $C = 88.3$; $H = 7.6$.

This substance represents the dihydroisobenzofuran derivative. It gives no addition compound with maleic anhydride, in concordance with the observation of Adams [50]. With conc. sulphuric acid, a curious reaction was observed. When 0.2 g. of the adduct and 1 cc. of sulphuric acid were heated to about 80°, complete solution took place, the colour changing from initial yellow with green fluorescence,
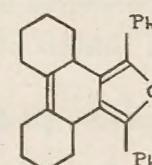
to red, then to brown. On pouring on to ice, a greyish powder was obtained, which can be satisfactorily recrystallized from ethanol or butanol. These solutions show no fluorescence at all. Sharp plates m.p. 141°. Unlike the adduct, the substance dissolves readily in petroleum ether. Yield quantitative.

Anal. Calcd. for $C_{28} H_{28} O$: $C = 88.4$; $H = 7.4$.
Found : $C = 88.3$; $H = 7.4$.

The substance is isomeric with the furane. Reaction with maleic anhydride gave unclear results. A structure like :
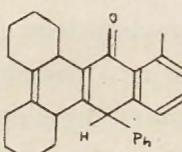
is to be considered. It is also possible that the substance contains the double bonds in other positions than in the normal adduct, but this point was not elucidated.

5) WITH BENZOYLACRYLIC ACID.—9. benzoyl, dodecahydrophenanthrene 10 carboxylic acid.

a) Dicyclohexenyl (8 g.) and trans-benzoylacrylic acid (10 g.) were heated together to 170/180° for 4 hours. The red syrup was treated with methanol and yielded about 4 g. of crystalline material = 24 %. From butylacetate plates : m.p. 258/9°. The substance is resistant to bromine.

Anal. Calcd. for $C_{22} H_{26} O_3$: $C = 78.$-; $H = 7.7$.
Found : $C = 77.9$; $H = 7.6$.

b) 10 g. of the diene and 12.5 g. of the acid in xylene (50 cc.) were boiled 7 hours and left overnight in an ice-box. Yield 4.5 g. of the adduct = 22 %.

c) The diene (3.2 g.) and the acid (3.6 g.) in ethanol (20 cc.) were boiled for 8 hours. Crystals appeared already during reaction. Yield 1.8 g. = 27 %.

The methyl ester of the adduct was prepared by means of diazomethane, it crystallizes from petroleum ether (130°) in clusters of needles, m.p. 159/160°.

Anal. Calcd. for $C_{23} H_{28} O_3$: $C = 78.4$; $H = 8.$-; $OCH_3 = 8.8$.
Found : $C = 78.4$; $H = 8.1$; $OCH_3 = 8.8$.

No esterification occured in boiling methanol with gaseous Hydrochlorid acid.

The adduct gave a clear, red-brown solution in conc. sulphuric acid. On pouring onto ice, a white precipitate is obtained, which can be recrystallized from methanol with huge losses m.p. 124/125°.

Anal. Calcd. for $C_{22} H_{23} O_4$: $C = 74.1$; $H = 7.9$.
Found : $C = 73.9$; $H = 7.5$.

This points to a hydrate of the adduct,

The adduct itself could not be cyclized by sulphuric acid in benzoylchloride to yield the corresponding derivative of 1. 2. 3. 4 dibenzanthraquinone [51]. Apparently this method is not suitable for partially hydrogenated o-benzoylbenzoic acids.

6) WITH BENZOQUINONE.—The diene (8 g. = 1/20 mol.) and the quinone (1.1 g. = 1/100 mol.) were warmed on a water bath for five hours. The clear solution started crystallization already after three hours. These crystals (2.5 g.) showed a m.p. of 235/240°. This substance is dimorphic. From butanol, it crystallizes, in prismatic rods m.p. 233/235°. From high boiling petroleum ether, in needles, m.p. 247°. The mother liquors deposited after 24 hours, a second crop (0.8 g.) of m.p. 190/195°. From high boiling petroleum ether clusters of rectangular prisms, m.p. 212°.

Anal. Calcd. for $C_{30} H_{40} O_2$: $C = 83.3$; $H = 9.3$.
Found : $C = 82.8$; $H = 9.2$.

On concentrating the mother liquors, a further crop (0.4 g.) of the first isomer m.p. 247° was obtained, bringing the total yield to 86 %.

Enolization : 0.5 g. of the isomer m.p. 247° was suspended in ethanolic potassium-hydroxide and left at room temperature for 24 hours. The filtered material was recrystallized, twice, from nitrobenzene. Clusters of colourless needles m.p. 327°. The substance was recovered, unchanged, after boiling its butanolic solution with ferric chloride.

Anal. Calcd. for $C_{30} H_{40} O_2$: $C = 83.3$; $H = 9.3$.
Found : $C = 83.3$; $H = 8.9$.

The isomer m.p. $212°$ gave under the same treatment an isomeric enol, in colourless needles (from butyl acetate) m.p. 310-$312°$.

Anal. Calcd. for $C_{30} H_{40} O_2$: $C = 83.3$; $H = 9.3$.
Found : $C = 83.5$; $H = 9.6$.

According to Barnett [52], a solution of quinone (0.6 g.) in dicyclohexenyl (2 g.) was boiled for 2 minutes and the mixture treated with alcohol and acetone. From butyl acetate, white needles were obtained (0.2 g. = 10 %) m.p. $308°$; mixed m.p. with the isomer m.p. $310/312°$ gave m.p. $308/310°$. The mother liquors were concentrated and yielded, upon treatment with ligroine, 0.1 g. of a mixture of the isomers m.p. $247°$ and m.p. $212°$.

7) WITH α NAPHTHOQUINONE.—The quinone (1.2 g. = 1/130 mol.) and the diene (6 g. = 1/26 mol.), when heated on a water bath, gave a clear solution, which solidified already after 2 hours. Treatment with alcohol gave 2.5 g. (100 %) of the adduct which recrystallized, from butanol, in colourless plates m.p. $207/208°$.

   a) 0.5 g. of the adduct was suspended in hot alcohol and alcoholic potash added; the solution turned immediately red-yellow, and, on cooling, a red solid crystallized. On recrystallization, first an inhomogeneous material (yellow needles, red prismatic rods) appeared, which, however, gradually changed into a pure red substance. Prismatic rods (from butyl acetate) m.p. $248°$.

Anal. Calcd. for $C_{22} H_{22} O_2$: $C = 83.$ -; $H = 6.9$.
Found : $C = 82.7$; $H = 7.1$.

   b) 0.5 g. of the adduct m.p. $207/208°$ was dissolved in glacial acetic acid (25 cc.) and at $80°$ five drops of conc. hydrogen bromide were added. The colourless solution turned immediately yellow and deposited, on cooling, yellow needles. From acetic acid, m.p. and mixed m.p. with a previous sample [53], m.p. 234-$235°$ conc. sulphuric acid gave a beautiful red colour.

Anal. Calcd. for $C_{22} H_{20} O_2$: $C = 83.6$; $H = 6.3$.
Found : $C = 83.8$; $H = 6.1$.

From the acetic acid filtrate, water precipitated a brown-black material (probably a quinhydrone compound) repeated recrystallization from butyl acetate gave red rods corresponding to the enol compound m.p. $248°$.

8) WITH FUMARIC ACID.—The acid (1.25 g. = 1/92 mol.) suspended in the diene (8.5 g. = 1/18 mol.) did not react at $100°$. However, reaction took place at $190°$-$200°$. The excess of the diene was distilled off, and the residue extracted with boiling sodium hydroxide solution. The adduct acid, which was precipitated from the filtered extract, was amorphous (2.5 g. = 80 %) and therefore converted into its dianilide. The adduct was dissolved in benzene (25 cc.) and phosphorus pentachloride (2.2g.) added at once. An exothermic reaction occurred and was completed by refluxing for half an hour. Solvent and phosphorus oxychloride were removed in vacuo, and the residue boiled with aniline (2 cc.), for 2 minutes. Hydrochloric acid precipitated a sirupy product, which crystallized on treatment with alcohol. From acetic acid, long, colourless, slender needles m.p. $312°$.

Anal. Calcd. for $C_{28} H_{32} O_2 N_2$: $C = 77.8$; $H. 7.4$; $N. 6.5$.
Found : $C = 78.$ -; $H. 7.8$; $N. 6.8$.

9) WITH β NITROSTYRENE.—The philodiene (1 g. = 1/150 mol.) and dicyclohexenyl (5 g. = 1/30 mol.) were warmed, on a water bath, for 8 hours. On cooling, the product crystallized and was triturated with methanol. Yield 1.9 g. = 95 %. From butanol beautiful rods m.p. $187°$. With hot conc. sulphuric acid a golden yellow solution was obtained.

Anal. Calcd. for $C_{20} H_{25} O_2 N$: $C = 77.2$; $H. 8.$ -; $N. 4.5$.
Found : $C = 77.2$; $H. 8.3$; $N. 4.6$.

The adduct was not attacked by catalytic hydrogenation in accordance with observations of Alder [54]. (The C_2-C_3 double bond of the medium ring in these adducts is known to be entirely refractive.)

10) WITH DIBENZALACETONE.—The ketone (1.2 g. = 1/200 mol.) and the diene (4 g. = 1/40 mol.) were heated to $180/190°$ during 5 hours. The sirupy mass crystallized on trituration with ethanol (2 g. = 95 %). From butanol, thin long needles; m.p. $208/209°$.

Anal. Calcd. for $C_{41} H_{50} O$ (double adduct) : $C = 88.2$; $H. 9.$ -
Found : $C = 88.5$; $H. 8.6$.

GRIGNARD REACTIONS WITH DICYCLOHEXENYL ADDUCTS.

The designation of the adducts is made according to table V.

1) *Reaction of the methyl esters of I with methylmagnesium iodide.*—In etheral solution no reaction occurred. 2 g. of the ester of I_A m.p. 111° were added to a Grignard solution from methyl Iodide (4 g.) and magnesium (0.7 g.). After distilling off the solvent, the residue was heated on a steam bath for 10 hours. After the usual decomposition, the ether left a thick oil, which was induced to crystallization by methanol and a few drops of ethyl acetate. From ethanol needles m.p. 135°. The product is identical with the Ketone II_A.

The ester did not react with Phenylmagnesiumbromide in boiling xylene. The isomeric ester of I_B showed no reaction with either of the Grignard compounds.

2) *Reaction of the Ketone II_A with methylmagnesium iodide.*—The reaction was accomplished in boiling toluene and yielded a thick oil, b.p. 190/200°/4 mm. Yield 60 %.

Anal. Calcd. for $C_{23} H_{32} O$: $C = 85.2$; $H = 10. -$
Found : $C = 85.2$; $H = 10.4$.

The carbinol could not be cyclized by sulphuric acid in acetic anhydride.

3) *Reaction of Ketone II_A with phenyl magnesium bromide.*—The reaction must be carried out in boiling xylene. After decomposition of the mixture with sulphuric acid, we obtained directly an olefine IV. It was purified by vacuum distillation b.p. 190/200°/0.05 mm. Recrystallization from methanol and water yielded aggregated plates m.p. 106/107°.

Anal. Calcd for $C_{28} H_{32}$: $C = 91.3$; $H = 8.7$.
Found : $C = 91.3$; $H = 8.7$.

Bromine is eagerly absorbed, but the bromination product is an oil which could not be purified.

4) *Reaction of Ketones III with methyl magnesium iodide.*—0.5 g. of the adduct III_A and 5 equivalents of Methyl magnesium iodide in toluene, were heated in an oil bath for 10 hours. After the usual decomposition, the reaction product was distilled in high vacuum (0.05 mm.) bath temperature 280/300°. A drop of yellowish oil was obtained which could not be induced to crystallization. Because of the small

amount of material available, the oil could not be purified satisfactorily; therefore, no definite conclusion can be drawn regarding the sterical relation of Ketone II_A to III_A or III_B.

The same reaction was again carried out with the main isomer III_B m.p. 216°, and yielded IV_B m.p. 156°.

Anal. Calcd for $C_{28} H_{38}$: $C = 91.3$; $H = 8.7$.
Found : $C = 91.4$; $H = 8.6$.

FRIEDEL AND CRAFTS REACTION WITH ADDUCTS I.

Since the methyl ester of I_A m.p. 111° did not react to give with phenyl magnesium bromide the ketone III_A we tried this interconversion by means of the Friedel and Crafts reaction. The acid I_A m.p. 231° was converted to its chloride by means of phosphoruspentachloride [55] (one part to one part) in 30 parts benzene; after a half-hour heating on a steam bath, the solvent was driven off in vacuum not over 50°; some more solvent was added and, again, evaporated in vacuum. The remaining clear syrup consists mainly of the pure chloride and can be converted into its anilide by mixing with two parts of aniline. The rich precipitate, which is formed almost immediately, is washed with hydrochloric acid. From acetic acid, branched needles m.p. 307/308°.

Anal. Calcd for $C_{27} H_{31} ON$: $C = 84.2$; H. 8.1 ; N. 3.6.
Found : $C = 84.3$; H. 8.3 ; N. 3.9.

The isomeric adduct I_B m.p. 282° gave under the same conditions a lower melting anilide in form of clusters of needles m.p. 247/8°.

Anal. Calcd for $C_{27} H_{31} ON$: $C = 84.2$; $H = 8.1$.
Found : $C = 84. -$; $H = 8.2$.

Owing to the lack of material, only the chloride of I_A gave clear results in the Friedel and Crafts reaction.

To a boiling solution of benzene containing in suspension the aluminium chloride (10 g.). The acid chloride (8 g.), in benzene (30 cc.), was added dropwise. After

the evolution of hydrochloric acid, the solution became brown and homogenous; boiling was continued for one hour. After decomposition, with cold NaOH, the residue was distilled in vacuum and the crop passing at $260/320°/0.05$ mm., was collected ($-3-4$ g.) then triturated with acetic acid and left for 4-5 days till it showed tendency for crystallization. The mother liquors were decanted and the semi-crystalline residue kneaded with petroleum ether. The crystals were then filtered and melted at about $180°$ (1 g.). Recrystallization from petrol-ether gave fine needles m.p. $203/204°$ which did not look uniform under the microscope. However, it did not correspond to either III_A or III_B. On recrystallization, in isopropanol, most of the material dissolved leaving some indissolved needles melting at $204°$, and on cooling long needles deposited. This procedure was repeated three times until a pure product melting at $198.5/199.5°$ was obtained as long needles.

Anal. Calcd for $C_{27} H_{30} O$: $C = 87.6$; $H = 8.1$.
Found : $C = 87.3$; $H = 7.8$.

The same chloride when treated with Phenylmagnesium bromide in a Grignard reaction, gave an undetermined amorphous powder.

II. REACTIONS WITH BIS DIALINE.

Preparation of 3. 4, 3' 4' tetrahydro 1.1, binaphthyl (Bis-dialine).

For the preparation of tetralone, we used the method of Thompson [56]. Contrary to this author's experience, we did not find the described treatment sufficient to remove peroxides. Eventually the following changes were introduced. Treatment with NaOH at $60°$ was extended to 4 more hours, and shaking with ferrous sulphate at room temperature was extended, at least, for 24 hours. The average yield was $2/3$ of that reported by Thompson. Pinacolization of tetralone was best effected in the following way : To 200 cc. of dry benzene, 10 cc. of absolute ethanol were added, and about 25 cc. were distilled off. Thin aluminium foil (7 g.), was added, care being taken to expose a fresh surface of the metal, then 1 g. of mercuric chloride, and finally 20 g. tetralone were added. The mixture was refluxed overnight. The liquid was now decanted, the remaining metal dissolved in dilute HCl + ice, and the solution extracted with ether. The ether extracts were combined to the benzene sol., the solvents removed and the residue refluxed for 3 hours with a mixture 1 : 1

of acetic acid and acetic anhydride. On cooling, bis-dialine (15 g.) crystallized. Recrystallization from ethanol containing 10 % benzene gave 12 g. of pure diene m.p. $141°$. The pinacol itself when isolated crystallized from butyl acetate in beautiful prisms [52] m.p. $191-192°$.

1) *Condensation with maleic anhydride.*

a) The anhydride (24 g. = $1/4$ mol.) and bis-dialine (6 g. = $1/40$ mol.) were heated together on a water bath for 4 hours. The clear solution solidified completely. The excess anhydride was removed by water. The residue m.p. $233°$ (8 g. = 95 %) was fractionally crystallized from xylene. The main product forms thick rectangular plates m.p. $256°$.

Anal. Calcd for $C_{24} H_{20} O_3$: $C = 80.9$; $H = 5.6$.
Found : $C = 81.1$; $H = 5.5$.

The mother liquors yielded a second adduct; cluster of fine needles m.p. $260°$ mixed m.p. with the main isomer : $232°$.

Anal. Calcd for $C_{24} H_{20} O_3$: $C = 80.9$; $H = 5.6$.
Found : $C = 81.-$; $H = 5.6$.

The main product m.p. $256°$ was transformed into its dimethyl ester with diazomethane; from high boiling petroleum ether, tetragonal pyramides m.p. $168°$.
The ester (0.9 g.) was isomerized to the trans-form with sodium (0.5 g.) in boiling butanol (25 cc.) during 3 hours. The sodium salt of the isomeric acid crystallized on cooling. It was decomposed with dil. sulphuric acid at $0°$, and the product recrystallized from butyl acetate to give the trans dicarboxylic adduct, m.p. $239°$.

Anal. Calcd for $C_{24} H_{22} O_4$: $C = 77.-$; $H = 5.9$.
Found : $C = 76.7$; $H = 5.7$.

The isomeric adduct m.p. $260°$, on the other hand, resisted all attemps to convert it to the free di-acid. Therefore, its ester could not be obtained and the same chain of reaction could not be carried out here.

b) Condensation in nitrobenzene.—The diene (2.5 g.) and maleic anhydride (15 g.) were boiled in nitrobenzene 25 cc. After 3 hours, the product, which crystallized on cooling, was identical with the adduct m.p. 256°. Then boiling was extended to 10 hours. The solvent removed by steam and the black residue dissolved in 30 % aqueous KOH with addition of some alcohol, the extract boiled with charcoal and filtered. The filtrate was nearly neutralized with HC*l*, a small amount of tar, which settled down, was removed, and then, excess of HC*l* added. The orange-yellow product was recrystallized from ethylbenzoate (red solution with green fluorescence) m.p. 275° (Yellow icosihedra).

Anal. Calcd for $C_{24} H_{16} O_2$: C = 81.8; H = 4.55.
Found : C = 81.8; H = 4.2.

2) *With Benzoquinone.*

The diene (2.6 g.) and benzoquinone (11 g. = 10 eqv.) were heated together to 125/150° for 3 hours. At first, an homogeneous liquid resulted, which, however, solidified later completely. After steam distillation, a dark red residue was left. Crude yield = 3 g. (80 %). Recrystallization, from butyl acetate and acetic anhydride, gave red plates m.p. 268°.

Anal. Calcd for $C_{26} H_{18} O_2$: C = 86.2; H = 5.-
Found : C = 86.-; H = 4.7.

The substance was not altered, when treated with HB*r* in acetic acid solution. No addition was observed, when 4 eqv. of the diene were heated with 1 mol. of quinone, or when the components were dissolved in boiling benzene or xylene.

3) *With α Naphtoquinone.*

2 mols. of the quinone were heated with one mol. of the diene at 130° for 3 hours. After steam distillation the residue was triturated with chloroform-ethanol. From butanol, fine yellow needles m.p. 226°. Yield 50%.

Anal. Calcd for $C_{30} H_{24} O_2$: C = 86.5; H = 5.8.
Found : C = 86.6; H = 6.-

4) *With trans dibenzoylethylene.*

No reaction took place in boiling benzene. If, however, the diene (2 g.) and the ethylene (2 g.) were heated to 200° for 10 hours; about 2 g. (50 %) of yellow crystals were obtained by treating the reaction mixture with ethanol-acetone. From butylacetate, prisms m.p. 236/238°. Near the end of the crystallization a second isomer appeared in form of needles, which, however, was not isolated.

Anal. Calcd for $C_{36} H_{20} O_2$: C = 87.4; H = 6.1.
Found : C = 87.1; H = 6.4.

Isomerization : The adduct (1.7 g.) was dissolved in boiling acetic anhydride (25 cc.). When five drops of phosphoric acid were added, the colour changed from yellow to red. The product was recrystallized from nitrobenzene, then from acetic anhydride. Yellow prismatic rods m.p. 272/273°.

Anal. Calcd for $C_{36} H_{28} O$: C = 90.8; H = 5.9.
Found : C = 90.2; H = 6.-

When the product was dissolved in conc. $H_2 SO_4$ at 50°, no isomer analogous to the corresponding derivative of dicyclohexenyl could be detected.

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